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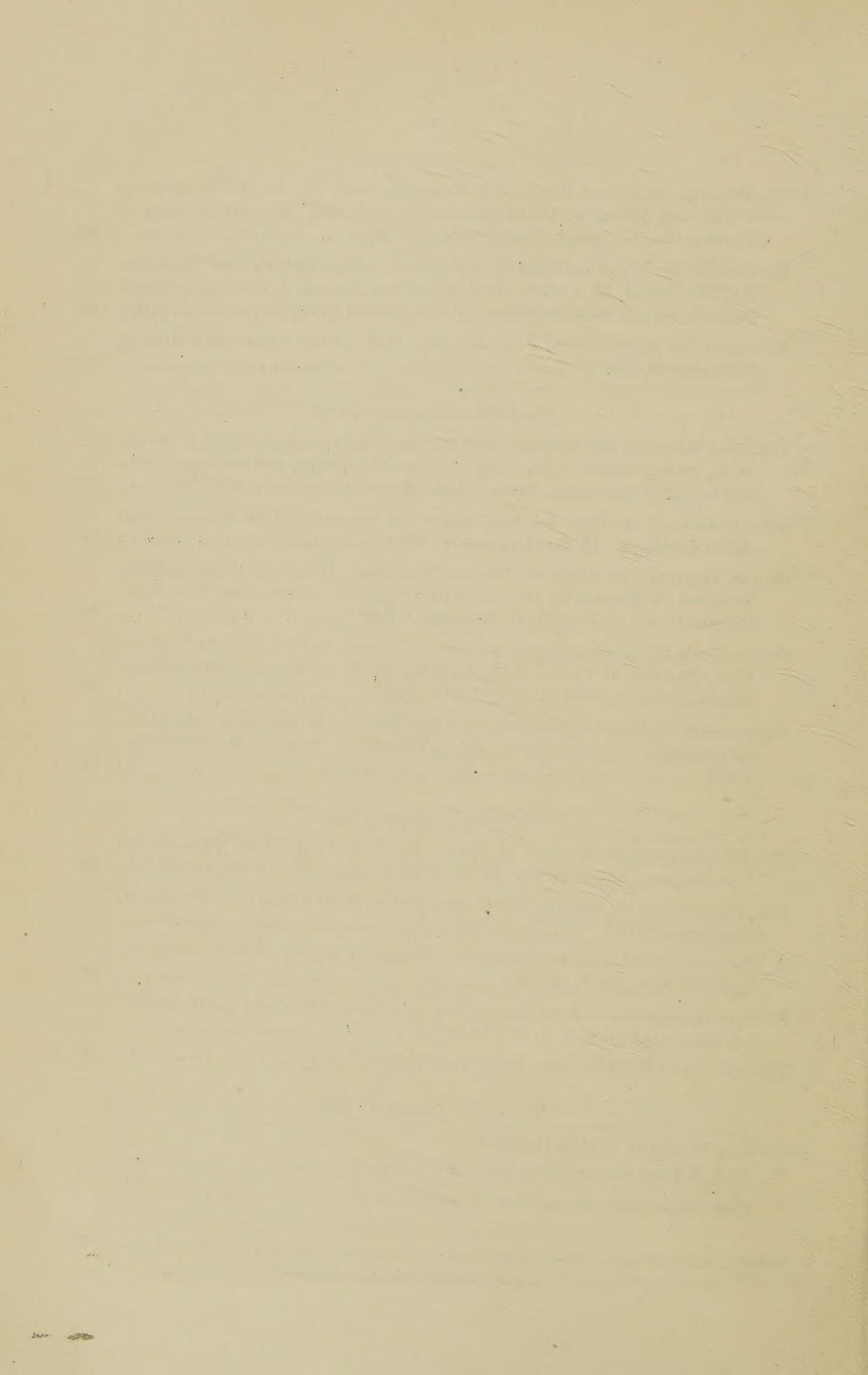
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PROCEEDINGS OF THE ROYAL SOCIETY.

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

The Aspherical Nucleus Theory applied to the Balmer Series of Hydrogen.

By L. SILBERSTEIN, Ph.D., Lecturer in Mathematical Physics at the
University of Rome.

(Communicated by Prof. J. W. Nicholson, F.R.S. Received April 16, 1920).

The purpose of the present paper is to apply the quantum theory of spectrum emission by atomic systems containing an *aspherical* nucleus, given in my recent paper,* to the Balmer series of hydrogen. Although, in working out the general formulæ of the said theory, I have had in view chiefly the more complicated, non-hydrogenic, spectra as a possible field of its application, yet it has seemed worth while to compare also the aspherical nucleus formulæ with the Balmer spectrum of hydrogen, the more so, as recent measurements have revealed a notable deviation of at least the first six members of this series from the simple Balmer formula. The measurements alluded to were made by W. E. Curtis in 1914, and their newly revised results are tabulated in his paper of 1919,† for a copy of which accompanied by helpful explanations, I am indebted to Prof. Fowler.

1. It will be sufficiently general for the purpose in hand to assume an *axially symmetrical* nucleus of unknown asphericity (to be determined from the observations). Then the series will be given by the formulæ (28), (28.1),‡ with $\kappa = 1$ (*i.e.*, nucleus charge = e), with $n' = 2$ written for the constant term, and $n = 3, 4, 5$, etc., for the members $H_\alpha, H_\beta, H_\gamma$, etc., of the series. Thus, if N be the Bohr value of the Rydberg constant, and if (retaining all other symbols of my quoted paper) we write for brevity

$$\sigma = \left(\frac{2Nch}{e^2} \right)^2 \cdot (A - B), \quad (1)$$

* "Spectra of Atomic Systems containing a Complex (*i.e.*, Aspherical) Nucleus,"

Phil. Mag., vol. 39, pp. 46-66 (1920).

† W. E. Curtis, 'Roy. Soc. Proc.,' A, vol. 96, pp. 147-155.

‡ *Loc. cit.*, p. 62.

the frequency formula will be

$$\nu = \frac{N}{4} \left\{ 1 + \frac{4\sigma g'}{(2-n'_3)^6} \right\} - \frac{N}{n^2} \left\{ 1 + \frac{n^2 \sigma g}{(n-n_3)^6} \right\}, \quad (2)$$

where $g = g(i, \epsilon)$ for the initial, and g' for the final orbit, are as on p. 55 (*loc. cit.*). It will be kept in mind that $A-B$,* and, therefore, σ , may be either positive or negative, according as the nucleus is "oblate" or "prolate" in the generalised sense of these words, as explained in the quoted paper. The variable number n is the sum of the three independent integers n_1, n_2, n_3 , introduced through the quantum integrals, and, similarly, $n' = n'_1 + n'_2 + n'_3$, the quantised eccentricity ϵ and inclination i of the electronic orbits, appearing in $g(i', \epsilon)$, being given by (21.3), *loc. cit.*

2. According to (2), every "member" or group of the series, such as $H_\alpha (n=3)$, will consist of many single lines or components. Let us call *main components* those lines in each group which correspond to the passage of the electron from a circular equatorial (initial) to a circular equatorial (final) orbit, *i.e.*, for $i = \epsilon = 0$ and $i' = \epsilon' = 0$. This corresponds to $n_2 = n_3 = 0$ and $n'_2 = n'_3 = 0$. Thus $n = n_1$, $n' = 2 = n'_1$, $g = g' = 1$, and the series of the main components will have (by 2) the frequencies

$$\nu = N \left\{ \left(\frac{1}{2^2} - \frac{1}{n^2} \right) + \sigma \left(\frac{1}{2^6} - \frac{1}{n^6} \right) \right\}, \quad (3)$$

where $n = 3, 4$, etc., for H_α, H_β , etc.

In the absence of better knowledge, and in a first attempt, let us correlate these frequencies of the *main components* with those measured by Curtis, and let us see whether the two constants N and σ can be determined so as to represent his observations by formula (3) with sufficient accuracy. At a later opportunity, we may try, if need be, to improve this correlation of theory with observation.

Curtis has measured only the first six members of the Balmer series, and his vacuum wave-lengths, in $\text{\AA}$, with their probable errors in $10^{-4} \text{\AA}$,† are

$H_\alpha (n=3).$	$H_\beta (4).$	$H_\gamma (5).$
6564.6022 ± 17	4862.6797 ± 10	4341.6830 ± 6
$H_\delta (6)$	$H_\epsilon (7)$	$H_\zeta (8)$
4102.8915 ± 13	3971.1940 ± 16	$3890.1489 \pm 11,$

and the corresponding frequencies ν are

$$15233.21_6 \quad 20564.79_3 \quad 23032.54_3 \quad 24373.05_5 \quad 25181.34_3 \quad 25705.95_7,$$

with probable errors which are at once derivable from those of the λ .

* A, B are the (electrical) "moments of inertia" of the whole nucleus charge, as defined on p. 61, *loc. cit.* The dimensions of these constants, A, B , characterising the nucleus, are those of a squared length.

† *Loc. cit.*, pp. 148 and 151.

Let us determine N and σ by the method of least squares from *all six* observations, notwithstanding that the uncertainty of a coincidence between our "main" component and Curtis's observed "centre" is much greater in the case of the broad group H_α than in the remaining ones. The resulting Gaussian normal equations are

$$\begin{aligned} 0.25557314_3 N + 0.018845437 N \sigma &= 28030.95_6, \\ 0.018845437 N + 0.001413238_8 N \sigma &= 2066.9451_9. \end{aligned}$$

Whence the required two constants become

$$\left. \begin{aligned} N &= 109678.0_8 \\ \sigma &= +9.007 \cdot 10^{-5} \end{aligned} \right\}, \quad (4)$$

so that the hydrogen nucleus would be *oblate*.* With these values of the coefficients formula (3) gives $\lambda = 1/\nu$ which differ from Curtis's λ -values by the following amounts, $\Delta\lambda = \lambda_{\text{calc.}} - \lambda_{\text{obs.}}$,

H_α	H_β	H_γ
$10^4 \cdot \Delta\lambda = +36 (\pm 17)$	$+2 (\pm 10)$	$-13 (\pm 6)$
H_δ	H_ϵ	H_ζ
$-10 (\pm 13)$	$-6 (\pm 16)$	$+3 (\pm 11) \text{ I.A.}$

The agreement for H_β , H_δ , H_ϵ , H_ζ , is complete, the differences being considerably smaller than Curtis's (bracketed) probable errors. For H_α and H_γ the differences are about twice his probable errors; but even these are not unsatisfactory, being of different signs (+36 and -13), and the group H_α being so broad that two or three thousandths of Å.U. can perhaps be thrown upon his fixing not our main component, but a slightly different place of the group. In fact, Paschen† quotes, for H_α , $\lambda_{\text{air}} = 6562.797$, which is by 0.004 greater than Curtis's value, and gives $\lambda_{\text{vac}} = 6564.606$, which agrees completely with our calculated λ (this being 6564.605_3). For H_β , Paschen's wave-length is identical with Curtis's value, but, for H_γ , Paschen quotes $\lambda_{\text{air}} = 4340.465$ (which is by 0.002 smaller than Curtis's value), giving $\lambda_{\text{vac}} = 4341.681$, and thus almost annihilating the above $\Delta\lambda$ for H_γ .

Under these circumstances, the agreement of (3), (4) with observations will be found better than might be expected, especially as the six differences $\Delta\lambda$

* If H_α is (in view of its excessive breadth) discarded from the least-square calculation, the result is $N = 109678.07$, differing but unessentially from the above value, and $\sigma = +9.638 \cdot 10^{-5}$. Curiously enough, these two coefficients give, with (3), for the main component of the excluded group H_α , $\nu = 15233.216$, identical in all eight figures with Curtis's value, which, of course, is a mere chance result. But these new values of N , σ make the $\Delta\lambda$ for the remaining five groups considerably greater, and, what matters more, all of the same sign (to wit, all negative).

† 'Annalen der Physik,' vol. 50, p. 935 (1916).

are irregularly distributed, and three are positive and three negative, giving $\Sigma\Delta\lambda = 41 - 29 = 12$, in 10^{-4} Å.U., if Curtis's observed λ are adopted throughout. With Paschen's values for H_α and H_γ , the agreement is, for all six groups, almost ideal.*

Ultimately, therefore, we shall retain the values of N and σ given under (4). These values will be used in (3) for the main components, and in (2) for all possible components of each group of the Balmer series.

3. *Comparison with Sommerfeld's Formula.*—Before proceeding with our subject, it may be interesting to see to what extent Curtis's observations can be represented by Sommerfeld's relativistic formula, which is based on the usual assumption of a spherical nucleus ($\sigma = 0$) and a variable mass of the electron. Sommerfeld himself does not seem to have tested his formula extensively enough in this respect. It is true that he gives† a comparison of his theoretical values of ΔN , the difference of the Rydberg constant in passing from H_α to H_β , or to H_γ , or H_δ , with observation. But, first of all, the "corrections" made for this purpose on the observed wave-lengths are avowedly conjectural and by no means binding; and, secondly, even if these be granted, the agreement between his theoretical figures

$$10^6 \frac{\Delta N}{N} = \begin{array}{ccc} H_\alpha - H_\beta & H_\alpha - H_\gamma & H_\alpha - H_\delta \\ 0.61 & 0.89 & 1.04 \end{array}$$

and the corrected observed ones,

$$\begin{array}{ccc} 0.37 & 0.35 & 0.06 \end{array}$$

is certainly not very reassuring. Under these circumstances, a comparison with Curtis's observations will not be out of place in our present connection.

Sommerfeld's frequency formula for the "main," *i.e.*, the circular-circular components is

$$\nu = N \left\{ \left(\frac{1}{2^2} - \frac{1}{n^2} \right) + a^2 \left(\frac{1}{2^4} - \frac{1}{n^4} \right) \right\}, \quad (S)$$

where a^2 is Sommerfeld's "universal" constant (not free as our σ), given by

$$a = \frac{2\pi e^2}{ch},$$

so that the coefficient of the correction term in (S) is essentially positive and, within narrow limits, fixed in its value. The value adopted by Sommerfeld, based on $e = 4.76 \cdot 10^{-10}$, $h = 6.51 \cdot 10^{-27}$, is $a^2 = 5.30 \cdot 10^{-5}$.

Now, using (S) and determining N and a^2 , again by the method of least squares, from Curtis's six observations, exactly as in the case of our formula (3), I find

$$N = 109677.67 \text{ and } a^2 = 3.390 \cdot 10^{-5},$$

and these coefficients, substituted in (S), give for $\Delta\nu = \nu_{\text{calc.}} - \nu_{\text{obs.}}$, for H_α up to H_δ , the values

$$\Delta\nu = -0.020 \quad -0.012 \quad -0.005 \quad -0.009 \quad -0.014 \quad -0.022, \quad (S)$$

* It may be argued that Mr. Curtis has represented all his six observations still better, to wit, by his formula (I), p. 148, *loc. cit.* But in this formula, which is of the Rydberg type, the two constants $\mu = +0.0,210$ and $p = -0.0,383$ do not seem to have an immediate physical meaning.

† 'Ann. d. Physik,' vol. 51, pp. 1-94 (1916).

‡ *Loc. cit.*, pp. 60-61.

which compare very disadvantageously with our differences corresponding to (3), (4), namely,

$$\Delta\nu = -0.009 \quad -0.001 \quad +0.007 \quad +0.006 \quad +0.004 \quad -0.002. \quad (3, 4)$$

The latter (aspherical) $\Delta\nu$ are considerably smaller and of different signs, whereas Sommerfeld's formula gives all $\Delta\nu$ negative. Moreover, the required value $a^2 = 3.39 \cdot 10^{-5}$ is much too far from Sommerfeld's $5.30 \cdot 10^{-6}$ to be admissible.*

This, however, is by no means intended to depreciate the value of Sommerfeld's beautiful theory, which in the eyes of the present writer is one of the most admirable works in modern physics.† But the chief experimental triumphs of Sommerfeld's theory seem to lie in the fine-structure of "lines" (or groups), more especially those of Fowler's principal series of (ionised) helium. Notwithstanding these notable successes in the case of the helium lines, we must keep an open mind in judging Sommerfeld's theory with regard to our present or to any other case.

4. By what has been said in Section 2, we have good reasons for attributing to the atom of hydrogen, as far as its Balmer series is concerned, the Rydberg constant given under (4), and an *oblate* nucleus, of which the amount of asphericity is given by

$$\sigma = \left(\frac{2Nch}{e^2} \right)^2 \cdot (A-B) = +9.007 \cdot 10^{-5}. \quad (4a)$$

It may be interesting to estimate, according to this formula, the difference $A-B$ of the principal "moments of inertia" of the hydrogen nucleus. Putting, in round figures,

$$N = 1.10 \cdot 10^5, \quad e = 4.76 \cdot 10^{-10}, \quad h = 6.51 \cdot 10^{-27}, \quad c = 3 \cdot 10^{10},$$

$$\text{I find} \quad A-B = 2.51 \cdot 10^{-21} \text{ cm}^2. \quad (4b)$$

To form an idea of the meaning of this result, suppose the nucleus to be a homogeneous rotational ellipsoid of axes $2a$ and $2b$, the former of these being the axis of symmetry. Then (*cf.*, *loc. cit.* p. 63) $A = \frac{2}{5} b^2$, $B = \frac{a^2 + b^2}{5}$, and

$$A-B = \frac{1}{5} (b^2 - a^2),$$

so that the nucleus is oblate in the usual sense of the word. If ζ be the eccentricity of the generating ellipse, we have $b^2 - a^2 = b^2 \zeta^2$, and, therefore,

* It may be interesting to mention in this connection that a much smaller deviation from this "universal" a^2 -value (to wit, 6.37 as against 5.30) has sufficed to K. Glitscher, a pupil of Prof. Sommerfeld, to condemn categorically Abraham's rigid electron in favour of Lorentz's deformable (*i.e.*, the relativistic) one. Cf. Glitscher's paper in 'Ann. d. Physik,' vol. 52, p. 608 (1917), or the account of it given in my 'Report on the Quantum Theory of Spectra,' London, Hilger, 1920.

† The "objections" against Sommerfeld's theory, hinted at in a footnote, p. 47 of my 'Phil. Mag.' paper (cited before), were found to be only apparent difficulties concerning the "canonical" nature of Sommerfeld's variables. This point has, in the meantime, been completely explained by Sommerfeld in a private communication to the author.

by (4b), $b^2\zeta^2 = 5(A-B) = 1.26 \cdot 10^{-20}$, i.e., for the product of the eccentricity into the major semi-axis of the nucleus,

$$b \zeta = 1.12 \cdot 10^{-10} \text{ cm.} \quad (4c)$$

This is, comparatively speaking, surprisingly large. For it would mean, for the equatorial semi-axis of the nucleus, at any rate,

$$b \geq 1.12 \cdot 10^{-10} \text{ cm.,}$$

the lower limit being reached for a nucleus flattened down to a disc, and, even then, its lateral dimensions would be scarcely as much as 100 times smaller than those of the whole hydrogen atom, or better, of the smallest stationary electronic orbit. Yet, the unexpectedly large value of $A-B$ or of $b\zeta$ does not seem to constitute a serious objection against the proposed theory. If, as is assumed by Rutherford, the mass of the nucleus is wholly electromagnetic, and its shape is spherical or almost so, then, of course, its dimensions would be of the order of 10^{-16} cm. But there is certainly no evidence whatever for the purely electric nature of the nucleus (nor for its spherical form). And, although Rutherford's scattering experiments are interpreted as pointing to nucleus dimensions of the order of 10^{-12} cm., or even 10^{-13} cm., yet the elementary theory of Rutherford's experiments is in many instances in direct opposition to observation,* so that the low-dimension figures often quoted after Sir Ernest Rutherford do not seem to be definitely established.

5. *Fine-Structure of H_α .*—For the first member of the Balmer series, the group H_α , we have to substitute in equation (2)

$$n = n_1 + n_2 + n_3 = 3,$$

so that the equation for the whole group will be

$$\frac{\nu}{N} = \frac{1}{4} \left\{ 1 + \frac{4\sigma g'}{(2-n_3')^6} \right\} - \frac{1}{8} \left\{ 1 + \frac{9\sigma g}{(3-n_3)^6} \right\}, \quad (5)$$

where, as for every group of the series, $n' = n_1' + n_2' + n_3' = 2$. For the main component of H_α we have

$$\frac{\nu}{N} = \frac{1}{4} \left\{ 1 + \frac{\sigma}{2^4} \right\} - \frac{1}{8} \left\{ 1 + \frac{\sigma}{3^4} \right\}. \quad (5_0)$$

Let us count the frequency distance $\delta\nu$ of any component of the group from the main component (and, similarly, their wave-length distances $\delta\lambda$). Then, subtracting (5₀) from (5), we shall have, for any component of the group H_α ,

$$\delta\mu \equiv \frac{\delta\nu}{N\sigma} = \frac{g'}{(2-n_3')^6} - \frac{g}{(3-n_3)^6} - \frac{1}{2^6} + \frac{1}{3^6}. \quad (6)$$

* See, for instance, 'Phil. Mag.', vol. 37, p. 553, table (1919).

The fine-structure of the whole group is thus seen to depend on N, σ only through their product, which, by (4) is, to three significant figures,

$$N\sigma = 9.88 \text{ cm.}^{-1}. \quad (7)$$

Since it is for the present futile to think of determining the distances of the components to within 1 per cent., we may as well take $N\sigma = 10 \text{ cm.}^{-1}$.

It is scarcely necessary to say that our fine-structure formula (6), and, similarly, those for H_β, H_γ , etc., are entirely different from Sommerfeld's formulæ.

Passing to the evaluation of the numerous arithmetically possible components determined by (6), it may be well to adopt a short symbol for each of them. As such we will take

$$\frac{n_1 n_2 n_3}{n_1' n_2' n_3'}$$

which will stand for the component due to the passage from the orbit n_1, n_2, n_3 to n_1', n_2', n_3' . Thus the main component of the group will be $\frac{300}{200}$. Similarly we shall write $\frac{210}{200}, \frac{210}{110}$, and so on. The sum of the upper numbers will be 3, and that of the lower numbers, 2.

Notwithstanding the smallness of the totals ($n = 3, n' = 2$) in the case of H_α , there is still quite a multitude of components arithmetically possible. Our first task must be to reduce their number, avoiding, however, as much as possible, any arbitrary assumptions.

In the first place, since the angular momentum corresponding to any stationary orbit is*

$$p = (n_1 + n_2) \frac{h}{2\pi},$$

and, since rectilinear orbits are not in question, we shall have to consider only such combinations of the two triads of numbers, for which

$$\left. \begin{aligned} n_1 + n_2 &> 0 \\ n_1' + n_2' &> 0 \end{aligned} \right\}. \quad (I)$$

In the second place, it will be remembered† that the full expression for the function g appearing in our formula is

$$g = g(i, \epsilon) = 1 + \frac{3}{2}\epsilon^2 - \frac{3}{2}\sin^2 i \cdot [1 + \frac{3}{4}\epsilon^2(1 + 2\sin^2 \omega)],$$

and, since the perihelion longitude ω is not quantisable, all components for which *both* the inclination i and the eccentricity ϵ of the initial or the final orbit differ from zero, will be more or less *broad* bands, according to the amount of inclination and eccentricity. Now, even if such components or

* *Loc. cit.*, p. 54.

† *Loc. cit.*, p. 55.

bands were equally probable as the remaining ones, *i.e.*, if the same numbers of individual atoms were engaged in producing them, yet, their light contributions being spaced all over the broad interval, corresponding to $\omega = 0$ to 2π , these bands will be much fainter than the sharp lines, in most cases, in fact, producing only a faint, hazy background to the whole group of sharp lines. At any rate, these broad components would be scarcely distinguishable, the more so as many of them overlap, as is shown by detailed calculations, which here may be omitted.

We shall, therefore, retain only *the sharp components*, *i.e.*, such only for which either n_2 or n_3 (or both) and at the same time either n_2' or n_3' (or both) vanish.* We can express this restricting condition shortly by requiring

$$\left. \begin{aligned} n_2 n_3 &= 0 \\ n_2' n_3' &= 0 \end{aligned} \right\}. \quad (\text{II})$$

This will greatly reduce the number of possible arithmetical combinations. At the same time the function g will be simplified down to

$$g = 1 + \frac{3}{2}(\epsilon^2 - \sin^2 i),$$

where, by (II), either ϵ or i (or both) vanish. Remembering that

$$\cos i = \frac{n_1}{n_1 + n_2}, \quad \epsilon^2 = 1 - \left(\frac{n_1 + n_2}{n} \right)^2,$$

we shall have, ultimately,

$$g = 1 + \frac{3}{2} \left[\frac{n_1^2}{(n_1 + n_2)^2} - \frac{(n_1 + n_2)^2}{n^2} \right], \quad (8)$$

valid for the sharp components of any member of the series. For the group H_a we have to put here $n = 3$, and similarly (for g') $n' = 2$.

We may subsequently consider a "selective principle," such as that given by Rubinowicz. But, in the meantime, let us consider the still numerous components left by the application of the conditions (I) and (II) alone, in short, *all sharp components* of the group H_a .

These, classified according to the final orbits (in rows, and initials in columns) are:—

$$\left. \begin{array}{cccccc} \overline{300} & \overline{210} & \overline{201} & \overline{120} & \overline{102} & \overline{030} \\ \overline{200} & \overline{200} & \overline{200} & \overline{200} & \overline{200} & \overline{200} \\ \overline{300} & \overline{210} & \overline{201} & \overline{120} & \overline{102} & \overline{030} \\ \overline{110} & \overline{110} & \overline{110} & \overline{110} & \overline{110} & \overline{110} \\ \overline{300} & \overline{210} & \overline{201} & \overline{120} & \overline{102} & \overline{030} \\ \overline{101} & \overline{101} & \overline{101} & \overline{101} & \overline{101} & \overline{101} \\ \overline{300} & \overline{210} & \overline{201} & \overline{120} & \overline{102} & \overline{030} \\ \overline{020} & \overline{020} & \overline{020} & \overline{020} & \overline{020} & \overline{020} \end{array} \right\}. \quad (9)$$

* That is to say, orbits either equatorial or circular (or both).

The first is the main ($\delta\nu = 0$). In all we have 24 components, which may be considered as four "sextets."* The first, or the main, sextet can be shortly denoted by 2.0.0; similarly, the second by 1.1.0, and so on. A glance at equation (6) will suffice to show that all these sextets are obtainable from one another by a *rigid shift* along the scale of frequencies.† Thus it is enough to write down one of the sextets, say the first, and to indicate the rigid shifts which carry it as a whole to the position of the second, the third, and the fourth sextets.

According to (6) and (8), and since $g(2,0,0) = 1$, more generally $g(n,0,0) = 1$, the first sextet will be given by

$$\delta\mu = \frac{\delta\nu}{N\sigma} = \frac{1}{3^6} - \frac{g}{(3-n_3)^6}, \quad (2.0.0)$$

and the rigid shifts transforming this into the 2nd, 3rd, and 4th sextet will be, respectively,

$$\delta'\mu = \frac{g(1,1,0)-1}{2^6} = -\frac{9}{512}, \quad (1.1.0)$$

$$\delta'\mu = g(1,0,1) - \frac{1}{2^6} = +\frac{135}{64}, \quad (1.0.1)$$

$$\delta'\mu = \frac{g(0,2,0)-1}{2^6} = -\frac{3}{128}. \quad (0.2.0)$$

Thus, by (8) and (2.0.0), using our above value of $N\sigma$, passing to $\delta\lambda = -\lambda^2\delta\nu$, and ordering the components after their increasing wave-length, we have, in Å.U., for the first sextet

$$\begin{array}{cccccc} 0.3.0. & 1.2.0. & 2.1.0. & 3.0.0. & 2.0.1. & 1.0.2. \\ \delta\lambda = -0.0088 & -0.0078 & -0.0049 & 0 & 0.1163 & [+9.9289], \end{array} \quad (2.0.0)$$

and for the shifts carrying this sextet rigidly into the remaining three sextets, according to the last quoted values of $\delta'\mu$,

$$\delta'\lambda_{(0.2.0)} = +0.0998; \quad \delta'\lambda_{(1.1.0)} = +0.0748; \quad [\delta'\lambda_{(1.0.1)} = -8.9812].$$

Let us discard, for the present, the very eccentric, and therefore distant, component of (2.0.0), and the corresponding components of (0.2.0), (1.1.0), as well as the whole distant sextet (1.0.1), distinguished by square brackets. Moreover, in view of the actual limits of spectroscopic precision, let us retain but the third decimals of Å.U. Then the whole material can be written as follows (regardless of the provisional grouping into "sextets," which are now partly intermingled):—

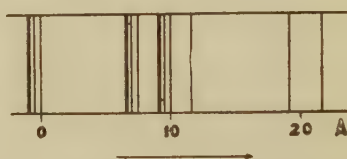
* If the reader prefers to classify them according to the initial orbits, he can consider the whole group, with equal right, as consisting of *six quartets*.

† At the same time we have six quartets, 3.0.0, 2.1.0, etc., following from one another by other rigid shifts.

Fine-Structure of H_α .

Component.	$\delta\lambda$ in Å.U.
030	-0.009
200	-0.008
120	
200	-0.005
210	
200	0.000
300	
200	+0.066
030	
110	0.067
120	
110	0.070
210	
110	0.075
300	
110	0.091
030	
020	0.092
120	
020	0.095
210	
020	0.100
300	
020	0.116
201	
200	0.191
201	
110	0.216
201	
020	

These are in all 15 components, of which those joined by brackets are so close together as to be scarcely separable from one another by available spectroscopic means. As such they are drawn on the accompanying figure.



We may now consider A. Rubinowicz's selective principle ("Auswahlprinzip"),* mentioned before. This requires "the azimuthal quantum number of an atom to jump at the utmost by a unit"; that number is in our (three-

* 'Physik. Zeitschrift,' vol. 19, pp. 441, 465. See also Chap. VI of Sommerfeld's book, just published, 'Atombau und Spektrallinien,' Brunswick, 1919.

dimensional) case $n_1 + n_2$, the factor of $h/2\pi$ in the value of the angular momentum, so that Rubinowicz's selective principle means

$$(n_1 + n_2) - (n_1' + n_2') = +1 \text{ or } -1 \text{ or } 0. \quad (\text{Rub.})$$

Now, although we have made no use of this well-founded principle in drawing up our list, it so happens that all the 15 components satisfy it, as a glance at the first column of the list will show.* The more advisable does it seem to retain, for the present at least, all these 15 sharp components of the H_α group. We may have to discard some of them on the evidence of further more precise measurements, which, as I learn from Dr. Merton, are now contemplated by him jointly with Prof. Nicholson.

For the present, little more can be said than that the above fine-structure is not contradicted by the available observations on H_α . In fact, what up to the present is known of this group is that it is separable into two conspicuous "components," 0.132 Å.U. apart,† the stronger component being the more red one. Now, in a first approximation (and especially in view of the light background due to the discarded broad components or bands) our first four theoretical components, together with the main which they so closely accompany, can be interpreted as the less red, and all the remaining, fused together, as the second, more red "component." The "centre" of the former can be taken to lie at $\delta\lambda = -0.005$, and that of the latter somewhere between 0.13 and 0.14, and this would give, roughly, the observed "separation of the two components," correct at least as to its order of magnitude. I understand from Dr. Merton's private communications that H_α is very likely to have a much more complicated structure than that usually described by a "doublet," a third component, in fact, appearing, under certain circumstances, between the two others. Also a suggestion made by Prof. Fowler would make it likely for H_α to be a typical triplet,‡ and this would answer better our configuration of components, in which there are two comparatively large gaps, one between 0 and 0.066, and another between 0.116 and 0.191. But a final verdict must be postponed until more precise experimental results are available. We will leave, therefore, for the present any further discussion of the fine-structure of the H_α group.

* Bohr's sharpened form of the selective principle excludes the *zero*, and thus would exclude our last three components. But, although certain cases speak for Bohr's principle, there are certainly no reasons for universalizing it.

† Buisson and Fabry, recently confirmed by Merton and Nicholson ('Phil. Trans.,' vol. 217, p. 275 (1917)), who find from 0.130 to 0.134 with a mean of 0.1323.

‡ Cf. Merton and Nicholson, *loc. cit.*, p. 262.

6. *Fine-structure of H_β .*—The equation of this group is, analogously to (6),

$$\frac{\delta\nu}{N\sigma} = \frac{g'}{(2-n_3')^6} - \frac{g}{(4-n^3)^6} - \frac{1}{2^6} + \frac{1}{4^6}, \quad (10)$$

with $n = n_1 + n_2 + n_3 = 4$. The final orbits will be as before. The initial ones will, of course, be more numerous. Classifying, again, all the components, which satisfy (I) and (II), according to the final orbits, we shall now have the octet 2.0.0,

$$\begin{array}{ccccccc} 400 & 310 & 301 & 220 & 202 & 130 & 103 & 040 \\ 200 & 200 & 200 & 200 & 200 & 200 & 200 & 200 \end{array}$$

and three more octets, 1.1.0, 1.0.1, 0.2.0, obtainable from this by the same rigid shifts as in the case of H_α . The whole group H_β would thus consist of 32 sharp components. Discarding, again, the very eccentric, and therefore very distant components, and proceeding in much the same way as before, we should still have as many as 21 components, whose $\delta\lambda$ range from -0.0009 to $+0.1335$ Å. Of these, however, unlike the previous case, the greater part infringes against Rubinowicz's selective principle. Discarding all these, to which belongs also the main itself $\frac{400}{200}$, the components $\frac{040}{200}$, $\frac{040}{110}$ and 12 others, we are left with only six sharp components satisfying Rubinowicz's principle, to wit,

$$\begin{array}{cccccc} \frac{301}{200} & \frac{301}{110} & \frac{301}{020} & \frac{202}{200} & \frac{202}{110} & \frac{202}{020} \\ \delta\lambda = +0.004_6 & 0.045_6 & \underline{0.059_4} & 0.078_7 & 0.119_8 & \underline{0.133_5} \text{ Å.} \quad (H_\beta) \end{array}$$

According to Bohr's rule,* one would still have to discard the two underlined components. But, in view of the incomplete experimental knowledge of the structure of this group, it will be best to leave the matter here for the present.

For the same reason it will be better to postpone also a desirable and possible retouching of the coefficients (4), and especially of N , in view of the manifestly *acentral* position of the main component within the theoretical group H_α as well as H_β , and presumably also H_γ , etc. Such a redetermination of N , σ might still improve the already good agreement of (3), (4) with Curtis's measurements.

* Which "prohibits" all combinations with $n_1 = 0$ or $n_1' = 0$. Cf. Sommerfeld's 'Atom bau,' etc., p. 451.

The Catalytic Activity of Copper.—Part I.

By W. G. PALMER, St. John's College, Cambridge.

(Communicated by Sir William Pope, F.R.S. Received May 31, 1920.)

There has been obtained, during recent years, a very great bulk of knowledge concerning the action of solid substances as accelerators or "catalysts" of chemical reactions taking place in the gaseous phase. Such catalytic actions include among their number processes for the production of sulphuric and nitric acids, for the manufacture of synthetic ammonia, and for the "hardening" of vegetable oils, and it is natural that the detailed investigation of this type of reaction should have been pursued mainly by industrial chemists anxious only to obtain the most efficient catalytic material by merely empirical methods. For this reason, and also because research upon catalytic actions presents certain peculiar experimental difficulties, the elucidation of the theoretical aspect of the subject is still tentative, owing to the lack of experimental quantitative data.

For a reaction accelerated catalytically, there will clearly be three parameters affecting the velocity of the reaction:—

- (i) The bulk concentration of the reacting substances.
- (ii) The temperature of reaction.
- (iii) The activity of the catalyst.

(i) and (ii) are general for all chemical reactions. The parameter (i) may be kept very approximately constant, while (ii) and (iii) are varied, by carrying out the reaction always in its "initial" state, that is to say, by passing the reacting substances over the catalyst at such a speed that at any time the concentration of the resultants of the reaction is negligible compared with that of the reactants.

It has been the object of the present work to discover in what way parameter (iii) depends on parameter (ii).

As is well known, the activity of the catalyst depends not only upon the temperature at which it is acting, but also on the mode of formation of the catalytic substance. For instance, it will be shown that pure metallic copper prepared by the electrolysis of solutions of copper salts has no catalytic activity of dehydrogenation upon alcohols, while the activity of copper prepared by reduction from its oxide depends on the temperature at which the reduction is carried out, and upon the reducing agent used.

The problem of standardising the mode of preparation of the solid catalyst

so that its activity should be reproducible in successive preparations, has proved a very serious difficulty to any study of the temperature coefficient of catalytic activity.*

The reaction chosen for study was the catalytic formation of acetaldehyde from ethyl alcohol by the action of copper. This reaction was studied qualitatively by Sabatier† and by Bouveault‡. Both these chemists agreed that up to a temperature of 300° C. the reaction is represented by the simple equation



and that no secondary reactions involving decomposition of aldehyde occur. This has been confirmed recently by Armstrong and Hilditch.§

The use of vapour from a boiling liquid as reactant simplifies the experimental conditions, as it is easy to regulate the rate of passage of the reactant over the catalyst by control of the heat supplied to the liquid. Moreover, complete purity is more easily secured in liquids than in gaseous reactants.

The catalytic activity of the metallic copper was found to decrease with use in spite of all precautions to ensure the purity of the reacting substances. The cause of this deterioration is still unknown, but suggestions are offered tentatively in the discussion at the close of the present paper.

In the present work the initial activity of the freshly prepared copper was measured and found to give concordant results in the sense that after the catalyst had been oxidised and reduced a second time the activity was of the same value as in the first instance.

The initial activity remained constant for at least one hour after the beginning of an experiment.

Experiments with Copper prepared Electrolytically.

It was thought that the difficulty previous workers have found in preparing a reproducible catalyst might be overcome by using as catalyst a cylindrical grid of metal gauze, coated with copper by electrolysis. Not only is the metal more easily prepared pure in this way than by the usual chemical processes, but if the activity became lessened with use, the copper could be readily dissolved off and a new catalytic surface formed under constant conditions of deposition.

Qualitative experiments were made in order to determine the conditions of deposition most suitable to this object. The surprising result was obtained

* Cf. Rideal, 'Trans. Chem. Soc.,' vol. 115, p. 995 (1919).

† 'Comptes Rendus,' vol. 136, pp. 738, 983 (1903).

‡ 'Bull. Soc. Chim. France,' [IV], vol. 3, p. 119 (1908).

§ 'Roy. Soc. Proc.,' A, vol. 97, p. 259 (1920).

that at no temperature between 200° C. and 300° C. is electrolytic copper, however prepared, catalytically active upon ethyl or isopropyl alcohols. As this result, although negative, may probably be of importance in a discussion of the mechanism of the catalytic action, a summary of the experiments made is now given.

The copper was deposited on a cylinder of fine silver gauze of diameter 1 cm. and length 10 cm. in the way recommended by Sand and Smalley for the estimation of copper.* After several holes of about 3 mm. diameter had been made in the gauze it was found easy to obtain an even deposit of metal both inside and outside the cylinder. The prepared contact material was supported by fine copper wires in the centre of an upright glass tube which could be electrically heated. The alcohol was placed in a flask directly connected with the lower end of the reaction tube, and was kept boiling by surrounding the flask with an oil-bath kept at 85° C. All stoppers were of cork, made gas-tight by well steeping in melted paraffin wax under reduced pressure.

The alcohol and condensible products of catalytic action were collected and tested qualitatively for acetaldehyde or acetone accordingly as ethyl or isopropyl alcohol was used. For the aldehyde a solution of magenta decolourised by sulphur dioxide was used; for acetone the distillate was allowed to stand for some time with *p*-nitrophenyl hydrazine. A small wash-bottle containing a small quantity of the alcohol used was attached to the outlet from the receiver, so that any evolution of uncondensable gas in the reaction could also be detected.

The isopropyl alcohol used in some experiments was prepared from acetone by reduction with hydrogen in the presence of nickel. The acetone was previously purified by Shipsey and Werner's method.†

The ethyl alcohol was dried over lime and refractionated before use to a range of 78·2°–78·3° C. Metallic calcium was not used to remove the last traces of the water from the alcohol, as it was thought that this metal, as ordinarily supplied, would introduce catalyst "poisons" into the alcohol.

The apparatus was tested gas-tight to a pressure of 12 inches of water before and after each experiment.

Sabatier (*loc. cit. supra*) observed 150° C. and 200° C. as the temperatures respectively at which copper reduced from its oxide began to react on isopropyl or ethyl alcohol.

(1) The electrolyte was prepared by dissolving 5 grm. of electrolytic copper foil in nitric acid, evaporating the solution and igniting the nitrate to

* 'Trans. Faraday Soc.,' vol. 6, p. 205 (1910).

† 'Trans. Chem. Soc.,' vol. 103, p. 1255.

oxide, which was then dissolved in 500 c.c. dilute sulphuric acid. 150 c.c. of the solution was taken for deposition; 1 c.c. concentrated nitric acid was added to the electrolyte. Deposition was carried out with 3·8–4·0 ampères at 3·3 volts and at a temperature of 60° C.

Before passing the alcohol over this preparation, the whole apparatus was filled with pure dry carbon dioxide by repeated exhaustion by the water pump. With isopropyl alcohol at 201° C. for five hours, no formation of acetone was observed.

(2) Contact material as in (1). The apparatus was filled with hydrogen, prepared by electrolysis of aqueous caustic potash, before experiment.

Isopropyl alcohol was unchanged after circulating at 290° C. for five hours.

(3) The copper used in (1) and (2) was removed from the silver gauze by dissolving it in dilute sulphuric acid containing hydrogen peroxide.*

Copper was then redeposited from electrolyte as in (1) at 4·7–4·8 ampères and 3·5 volts. The deposit was washed in boiling water for two hours, and left in a desiccator with soda-lime overnight.

The apparatus was filled with hydrogen as in (2). Isopropyl alcohol showed no change after circulating at 240° C. for four hours.

(4) The copper was deposited on the cleaned gauze at 60° C., with a reduced current of 1·5 ampères at 3·6 volts.

The deposit was first washed with cold water, and then with 3 per cent. sulphuric acid solution, and finally with distilled water.

The apparatus was filled with hydrogen. There was no action on isopropyl alcohol after heating to 280° C. for 3½ hours.

(5) The copper was deposited at a still lower current density, 0·5 ampère in the presence of sulphuric acid only. The temperature of deposition was 21° C.

Ethyl alcohol underwent no change by heating to 290° C. for four hours.

(6) During the removal of the copper in the above experiments, the silver gauze lost in weight, and became coated with finely divided silver. It was evident that the silver was becoming alloyed with the copper deposit at the temperatures to which this was heated.

All the experiments (1) to (5) were then repeated (also without observing any catalytic effect), using as support for the electrolytic copper a coil of ordinary copper gauze. This gauze was cleaned before use by boiling in dilute aqueous caustic soda and by making it the cathode in a cell containing dilute sulphuric acid.

(7) Copper was first deposited on the coil as in (5). The copperised gauze was then transferred to a bath of zinc hydroxide dissolved in caustic soda

* Sand and Smalley, *loc. cit.*

solution, and metallic zinc deposited for a short time upon the copper. The zinc was caused to become alloyed with the copper by finally heating to 300° C.

This contact material was not active on ethyl-alcohol at 284° C.

(8) The copper was deposited from Fehling's solution by a current of 0.5 ampère at 2.3–2.5 volts. The coil was allowed to stand overnight in distilled water before being used.

Before placing in the reaction tube the dry contact material was weighed. After ethyl alcohol had passed over this material at 295° C. for five hours without action, its mass was found not to have changed. The deposit, therefore, contained no cuprous oxide which is commonly found in copper deposited from alkaline solutions.

(9) Copper deposited from alkaline solution as in (8). Zinc was then deposited as in (7) but instead of alloying all the deposit with the copper by heating, it was assumed that a certain amount of alloying occurs during deposition; the detachable zinc was dissolved off in 3 per cent. sulphuric acid.

This preparation was not active on ethyl alcohol at 310° C.

(10) The surface of the coil used was so increased by successive wrappings after deposition as in (1) that it completely filled the reaction tube. Even under these conditions no reaction was observed at 320° C. with ethyl alcohol.

From the above series of experiments it is to be concluded that metallic copper, which has not been reduced from its oxide, has no dehydrogenating effect, even when alloyed with zinc.

Experiments with Copper Reduced from its Oxide by Hydrogen.

Determinations of acetaldehyde formed during a period of time will obviously be valueless unless some means is used to check the constancy of the catalytic activity at all times in the interval.

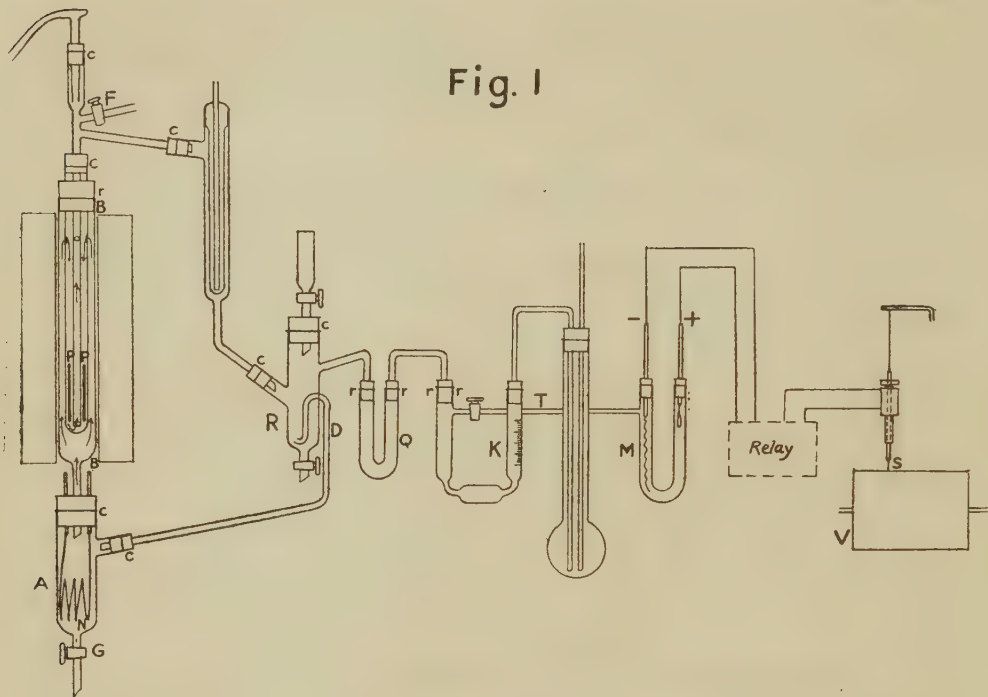
A simple method was devised of making the escape of hydrogen gas in definite units of volume self-recording on a chronograph. In the experiments to be now described the chronograph records were solely used to determine the catalytic activity. This method has the great advantage that any variation from constant activity during an experiment can at once be detected by inspecting the record.

Details of Apparatus (fig. 1).

The alcohol in the vessel A was kept boiling by means of a coil of nickel wire, N, heated electrically, the necessary platinum leads being copper-plated, to prevent possible extraneous catalytic action. The alcohol vapour passed

through the reaction tube, B, over the catalyst in the inner tube at PP (course shown in fig. 1 by means of arrows), condensing finally in the

Fig. 1

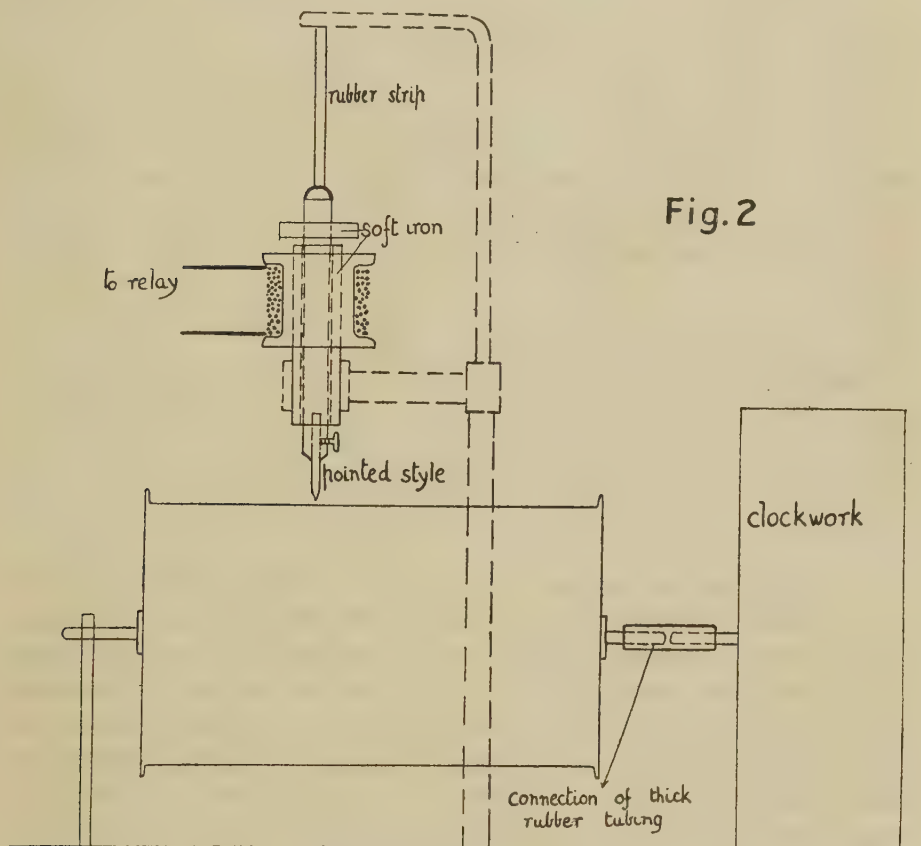


receiver, R. The liquid in R could be drawn back into A through a siphon-tube, D, if the current in the heating coil, N, were momentarily broken; thus opening of the apparatus and exposure of the contact material to air were avoided, and the amount of alcohol needed for a series of experiments was reduced. By plotting the current used to heat the coil, N, against the volume of liquid condensed in R in a given time, a curve was constructed showing the relationship between the heating current and the rate of passage of alcohol vapour over the catalyst.

The liquid condensed in R contained a small quantity of aldehyde, which, however, very rapidly boiled through the reaction tube after its return to A, so that only alcohol vapour passed into B after the first two minutes of distillation. At the close of a day's working, aldehyde was removed from the alcohol by boiling in a flask to which a simple bulbed tube was attached as condenser; through this the volatile aldehyde escaped, while the alcohol was condensed.

The hydrogen from the reaction-tube, after passing through the calcium chloride trap-tube, Q, reached the specially constructed escape-tube, K, the

right-hand limb of which was graduated in cubic centimetres. This tube contained a few cubic centimetres of water, the level of which rose and fell in the graduated limb at a rate corresponding with the production of hydrogen in B; the fall of liquid in the graduated limb followed on the escape of a definite volume of gas, read off by means of the graduations. By slightly tilting the escape-tube, variations of from 1–3 c.c. could be made in the unit at which escape of gas was possible.



The changes of level of liquid in K were imitated in the manometer, M, containing dilute sulphuric acid. An electrode of platinum wire descended into the acid in one limb of M; in the other limb, an electrode formed of a loop of platinum wire was so arranged that contact was made just as gas was about to escape from K. The momentary current so produced actuated a pointed steel style, S, so that it descended on the revolving drum, V, which was turned round once an hour by clockwork.

The manometer, M, was surrounded with ice, in order to avoid irregular

contacts caused by local heating of the sulphuric acid; the connecting tube, T, was of capillary bore, so that the fall of liquid in K might not cause oscillations of the liquid level and consequent irregular contacts in M.

The exit from K was guarded by a deep vessel, through which carbon dioxide was constantly flowing, so that in any accidental sucking back only this inert gas could pass into the apparatus.

The stoppers marked *c* were of cork, rendered gas-tight by waxing *in vacuo*; those marked *r* were of rubber; this material was not used where it would come into direct contact with liquid alcohol.

The temperature of the contact material was shown by a millivoltmeter in series with a copper-constantan thermo-couple, sheathed in a thin-walled glass tube to prevent extraneous catalytic action. This couple was calibrated for the range 100°–419° C. by using the known melting-points of various metals and the boiling-point of water as reference points.

An enlarged diagram of the recording part of the chronograph is shown in fig. 2.

Preparation of the Contact Material.

Electrolytic copper foil was dissolved in nitric acid, the solution evaporated to dryness and the residue ignited. The oxide so formed was dissolved in formic acid, and the formate twice recrystallised from aqueous solution.

Eight cylindrical rods of china clay, each of 3 × 80 mm. dimensions, were used as support for the catalyst. The composition of these rods was—

SiO ₂ = 65.27 per cent.	CaO = 0.43 per cent.
Al ₂ O ₃ = 30.06 "	K ₂ O = 1.61 "
Fe ₂ O ₃ = 0.65 "	Na ₂ O = 0.723 "
MgO = 0.173 "	

They were rendered inactive as catalysts by igniting to bright redness for four hours. The rods were then immersed in a cold saturated solution of the copper formate, and the pressure over the liquid reduced, by means of a water pump. After some time, the pressure was released, causing absorption of the liquid into the porous rods. This operation was repeated several times. The rods so impregnated were dried at 100° C. and then ignited at 300° C. in a current of air. They then showed a quite uniform coating of black cupric oxide, which could not be detached by rubbing; the oxide was, however, instantly removed by nitric acid. It is, therefore, probable that all the copper on the rods was active catalytically, as alcohol vapour could be expected to diffuse into the outer layers of the rods at least as quickly as nitric acid. An estimation of copper on spare rods prepared simultaneously

to those actually used as catalysts showed that the total amount of copper used as catalyst was about 1.2 gm.

Ethyl alcohol dried over quicklime was used. The fraction chosen boiled constantly at 78.10°C . (757 mm. pressure). The density $15^{\circ}/15^{\circ} = 0.7974$. Metallic calcium was not used for dehydrating the alcohol for the reasons mentioned above.

As in the experiments with electrolytic copper, the air in the apparatus was displaced by exhausting three times with a water-pump, and filling with pure dry carbon dioxide after each exhaustion.

The hydrogen used for reduction was made by electrolysis of caustic potash solution between nickel electrodes, and was dried with calcium chloride. Owing to the small quantity of copper oxide used, reduction took place in a very short time, so that a determination of catalytic activity could be made almost immediately after reduction. The hydrogen was allowed to flow into the reaction tube by opening the tap, F (fig. 1) and excess of gas issued from the lower tap, G.

Before any quantitative experiments were carried out the copper oxide was reduced at 250°C . and reoxidised again by air at 300°C . seven times successively.

Owing to the design of the apparatus, only 100 c.c. of alcohol were required even for an extended series of experiments. During the preliminary reductions of the copper oxide, this volume of alcohol was repeatedly passed over the copper, in order to remove possible catalyst "poisons."

After this preliminary treatment of the catalyst and alcohol, three quantitative experiments were made to find the extent of catalysis, and whether the catalyst was reproducible in successive reductions. A small wash-bottle containing alcohol kept cold in ice, and a guard-tube containing sodium bisulphite solution, were attached to the receiver, R, to collect the last traces of aldehyde not retained in the alcohol collected in R. The aldehyde was estimated by Ripper's method. Between each determination the catalyst was oxidised for about one hour at 300°C . with air.

The following results were found:—

Reduction by Hydrogen at 246°C .

Temperature of reaction.	Duration of experiment.	Acetaldehyde formed per hour.
246°C .	2 hours	0.46 gm.
245°C .	$1\frac{3}{4}$ hour	0.455 "
246°C .	1 "	0.450 "

It was therefore assumed that the catalyst had reached a steady, reproducible state, and a series of determinations with the chronograph were made.

After every determination of reaction velocity at a particular temperature, the catalyst was oxidised with a current of air at 300° C. In the first series of experiments (of which the results correspond to Curve I in the accompanying diagram) the reaction tube was filled with hydrogen before being heated. In the second series (Curve II) the reaction tube was slowly heated, and hydrogen passed in at a temperature of 204° – 206° C. In all cases the copper was heated after reduction to the desired temperature of reaction in a current of hydrogen.

The chronograph records were measured by counting and averaging the number of points over 1 inch of the chart (corresponding to 7.2 minutes), lengths being taken in several parts of the record. Records were usually taken for 30–60 minutes.

The reaction velocity was found to be independent of the rate of flow of the alcohol vapour over the catalyst between the limits 7–35 c.c. of liquid alcohol vaporised per hour.

Determinations of reaction velocity were made in deliberately haphazard order with respect to temperature, so as to eliminate possible unidirectional influences.

The following tables show the results obtained:—

Table I.—Catalyst from Copper Oxide reduced at the lowest possible Temperature by Hydrogen.

Numerical order of experiments.	Temperature ($^{\circ}$ C.).	C.c. of hydrogen per hour (from chronogram).
	°	(Volumes reduced to 0° C. and 760 mm. pressure.)
3	216	40.5
4	222	102
1	237	151
5	240	160
6	257	173
10	260	175
9	265	184
11	269	223
7	272	245
2	275	256

Table II.—Catalyst from Copper Oxide reduced at 205° C. by Hydrogen.

Numerical order of experiments.	Temperature (° C.).	C.c. of hydrogen per hour (from chronogram).
7	224	Very slight action only. 75 110 184 255 286
6	234	
2	250	
3	255	
1	270	
5	285	
4	300	

Discussion of Results.

If it is granted that pure metallic copper as obtained by the electrolysis of a copper salt is not catalytically active, two possible theories of the source of the activity in reduced copper seem to offer themselves :

(i) The activity is due to an oxide dissolved as a solid solution in the bulk of the metallic copper.

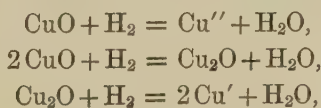
(ii) The activity is due to one or more labile forms of copper, which pass only slowly into stable inactive forms.

It should be possible to gain insight into the applicability of (i) or (ii) in the following way. The deterioration of the catalyst according to (i) would be due to a gradual reduction of the oxide to metal. The velocity at which this takes place should be markedly influenced by temperature, since the reaction would be strongly exothermic.

According to (ii), deterioration of the catalyst is due to a slow change labile form $\rightarrow$ inactive stable form. This change recalls allotropic changes, and might be expected to proceed without any marked heat effect; the rate of deterioration would hence be only slightly influenced by temperature.

Experiments based on these suggestions are now in progress. Certain experiments already carried out showed that the activity decreases smoothly with the time of use, after a period of one to two hours, during which the initial activity remained constant.

The reduction of copper oxide to metallic copper is very probably a complex reaction, resulting in the production of molecules of copper containing atoms of different valency. For example, the three reactions



probably proceed simultaneously when cupric oxide is reduced. The resulting copper consists of two types of molecules, one type composed of atoms of

cupric copper, and the other type of cuprous copper atoms. These two sorts of molecules would be heterotopic and possess different chemical properties,* and certainly very different surface lattices, and so exhibit different adsorptive characteristics.

The proportion of one type of molecule to another type would naturally depend on the reducing agent used and on the temperature at which reduction took place. The inactivity of electrolytic copper demonstrates the lack of catalytic power in molecules formed entirely of divalent copper. Experiments are now in progress to find the effect of reducing agents other than hydrogen upon the catalytic activity of the copper.

The Form of the Curves relating the Initial Catalytic Activity with Temperature.

So little work has been undertaken on the quantitative relations of the catalytic activity of the metals with temperature that material for comparison is almost completely lacking.

Grassitt† has determined the relation with temperature of the catalytic activity of copper as a hydrogenation agent, using ethylene as the reacting substance. In this reaction the activity appeared to reach a steady state only after the lapse of some time; the following numbers were obtained connecting the velocity of hydrogenation with temperature:—

Temperature °C.	Reaction velocity.
150°	0.25
200°	1.10
250°	1.19
275°	1.21

Armstrong and Hilditch (*loc. cit. supra*) have recently confirmed Sabatier's observation that no secondary products are formed when alcohol is dehydrogenated, provided the temperature is below 300° C. They observed, on the other hand, that when a mixture of hydrogen and aldehyde vapour is passed over copper at temperatures between 250° C. and 300° C. much of the aldehyde is destroyed by secondary action.

These facts are perhaps best interpreted by supposing that alcohol is selectively adsorbed by copper from a mixture of alcohol and aldehyde vapours, so that during dehydrogenation the surface of the copper is covered by a layer of alcohol molecules, and adsorption and consequent destruction of the aldehyde prevented.

* Soddy, 'Trans. Chem. Soc.,' vol. 115, p. 23 (1919).

† 'Nuovo Cimento,' vol. 11, pp. 147-163.

If it be supposed that dehydrogenation of alcohol involves three stages:—

- (i) Adsorption of alcohol molecules over the surface of the copper;
- (ii) Activation of certain alcohol molecules by absorption of energy;
- (iii) Evaporation of acetaldehyde and hydrogen away from the adsorption surface into the alcohol stream flowing past the catalyst;

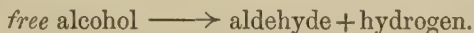
then this process bears a close physical analogy to the escape of ions from a heated solid. The products of dehydrogenation correspond to the ions liberated, while the immediate escape of these products into the gas stream corresponds to the attainment of "saturation current" by applying an E.M.F. to the thermionic system.

The velocity of formation of products of catalytic action should on this analogy be connected with absolute temperature by an equation of the form

$$K = A\sqrt{T} e^{\int^T \frac{\phi}{KT^2} dT^*}$$

where A is a constant, and ϕ = the work necessary to liberate one molecule of aldehyde and one molecule of hydrogen from one molecule of alcohol adsorbed on the copper surface.

ϕ is, of course, not necessarily the same as for the reaction



If ϕ is regarded as practically independent of temperature, this formula leads to curves with convexity towards the temperature axis, whereas the curves obtained in the present work show convexity towards the K axis. It seems, therefore, probable that ϕ is some function of T , but of what form it is at present impossible to determine.

The curve obtained by Grassi (*loc. cit.*) for the hydrogenation of ethylene by copper shows a very marked convexity towards the K axis.

Richardson† has shown that the form of the thermionic equation would not be materially altered if the molecule or atom became activated in quanta rather than continuously.

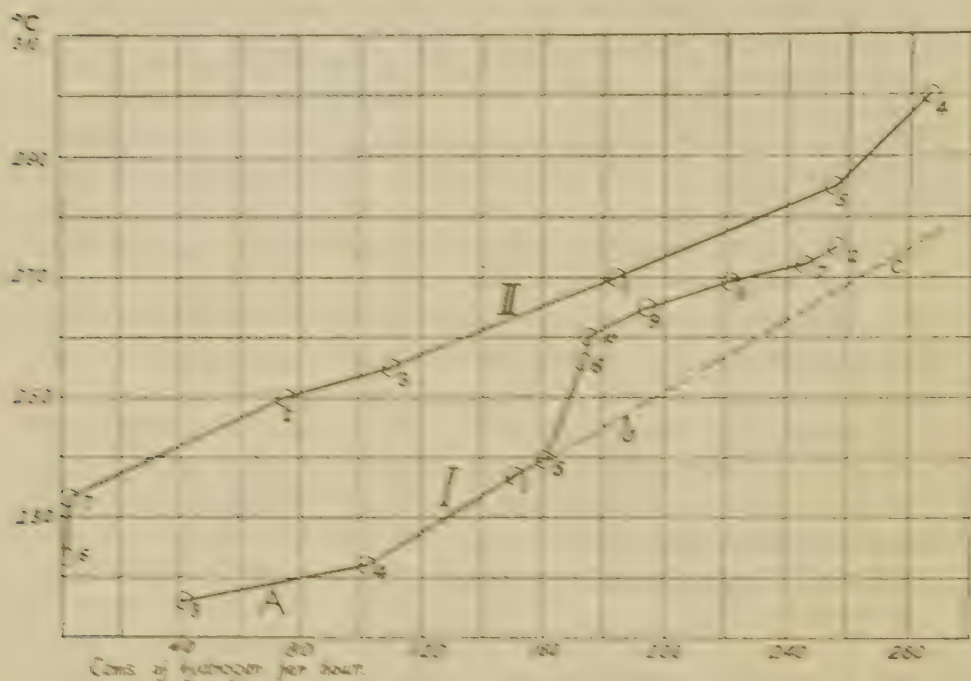
Curve I.—There is a sharp change in the direction of this curve between the temperatures 255° C. and 265° C.

The simplest explanation is to suppose that the "normal" curve for complete adsorption and subsequent dehydrogenation of alcohol should be Abc , which is roughly parallel to Curve II. At a temperature of 230° C. the activity begins to fall below the normal value, and continues to decrease to a minimum at about 260° C. The activity then reapproaches the normal

* Richardson, 'The Emission of Electricity from Hot Bodies,' p. 27, *et seq.*

† 'Phil. Mag.,' vol. 28, p. 633 (1914).

curve with increasing temperatures. This decrease and subsequent recovery of the activity is most probably to be attributed to the partial adsorption of



hydrogen and consequent decrease of the number of alcohol molecules per unit area of the catalyst.

It is striking in this connection that Grassi found (loc. cit. supra) practically a maximum for the hydrogenating activity at about 260° C. If aldehyde were adsorbed as well as hydrogen, secondary products might be expected in the products of reaction, which is not the case.

I am indebted to my wife for an analysis of the china-clay rods used to support the catalyst and for the preparation of pure isopropyl alcohol used in the experiments with electrolytic copper.

A Study of Catalytic Actions at Solid Surfaces. V.—The Rate of Change conditioned by a Nickel Catalyst and its Bearing on the Law of Mass Action.

By E. F. ARMSTRONG, D.Sc., F.R.S., and T. P. HILDITCH, D.Sc.

(Received June 3, 1920.)

In recent communications attention has been drawn to the analogy between the action of enzymes, which are essentially colloidal organic catalysts and of metallic catalysts, such as nickel, both of which are active in virtue of their surface at which the chemical action takes place.

It is possible to study the behaviour of the nickel catalyst with considerable accuracy under a variety of conditions, so that the opportunity is afforded of investigating the laws governing the rate of action in its presence, and comparing the results with those obtained with enzymes.

It may be stated at once that the results confirm the theory outlined by one of us in 1904, which, though accepted at the time, has subsequently been overlooked by adherents of the more generally accepted logarithmic theory of mass action.

In discussing the action of enzymes on sugars it was considered that the *active mass*, in more modern language the *adsorbed quantity*, is that proportion of the total sugar combined with the enzyme which is undergoing change at any one moment. When the active mass is small compared with the bulk concentration of the sugar, that is when the adsorption capacity is high and the surface is saturated with the active molecules, the rate of decomposition, $dx/dt = K$, over a considerable range of concentration becomes a constant, and equal weights of sugar are hydrolysed in equal intervals of time. To attain this result, it is necessary to have the enzymes so prepared as to be in a highly active state, and the conditions of the experiment so arranged that other disturbing factors do not arise. There is then no difficulty in realising in practice a linear rate of action, the duration of the linear phase of the change being the longer the greater the activity of the enzyme.

Originally the experiments were made with so-called soluble enzymes which, although colloidal, were believed to be in solution; in later years, they have been repeated with the same enzymes in an insoluble form, under conditions such that the hydrolyte must have been adsorbed by the enzyme and the action at the surface. Such insoluble enzymes are prepared by autolysing fresh leaves or suitable living material in presence of toluene, and completely washing away all soluble constituents; the residue is dried and

ground to a powder, which is often highly active towards β -glucosides, though aqueous extracts made from it are inactive.

The apparent logarithmic rates of action observed by some workers in enzymic changes are considered to be due to secondary changes, such as the combination of the enzyme with one of the products of change; in other words, a progressive diminution of the amount of enzyme available for hydrolysis. It is possible, when dealing with the hydrogenation of liquids in presence of nickel, to select conditions which are analogous to several of those which tend to confuse the simple, regular rate of hydrolytic action. The relation between the normal linear progression and the logarithmic rate of change induced by secondary causes then becomes exceedingly clear.

This result has been obtained by studying the rate of hydrogenation of a number of simple ethylenic compounds of the aromatic series, the absorption being measured by means of meters placed before and after the hydrogenation apparatus, as described in our first communication. Under the conditions of the experiments, the benzenoid residues present were not susceptible to hydrogenation.

Linear Character of the normal Hydrogenation Curves.

In the first place, owing to the small proportion of nickel compared to the amount of unsaturated compound (which involves a still smaller proportion present at any given moment of the unstable complex—nickel-ethylenic compound), the active mass undergoing change at any one moment is practically the same over a considerable period, and linear curves corresponding to the relation $K = v/t$ are obtained for 50–80 per cent. of the graph representing the complete hydrogenation.

We have obtained data of this in the case of the methyl and ethyl esters of cinnamic acid, $C_6H_5.CH:CH.COOH$, and the phenolic ethers anethol, $CH_3O.C_6H_4.CH:CH.CH_3$, and safrol, $CH_2O_2.C_6H_3.CH_2.CH:CH_2$, in hydrogenations conducted at 140° and 180° C. in presence of 0.15 per cent of nickel.

Figs. 1 and 2 show the graphs representing the results obtained; the numerical data are given for the typical case of methyl cinnamate, with the experimental values for $K = v/t$ (linear relation) and $K' = \frac{1}{t} \log \frac{V'}{V' - v}$ (unimolecular mass-action equation, V' , being the volume of hydrogen required to saturate 100 grammes of methyl cinnamate). The figures for the other compounds are closely similar and need not be given *in extenso*.



FIG. 1.

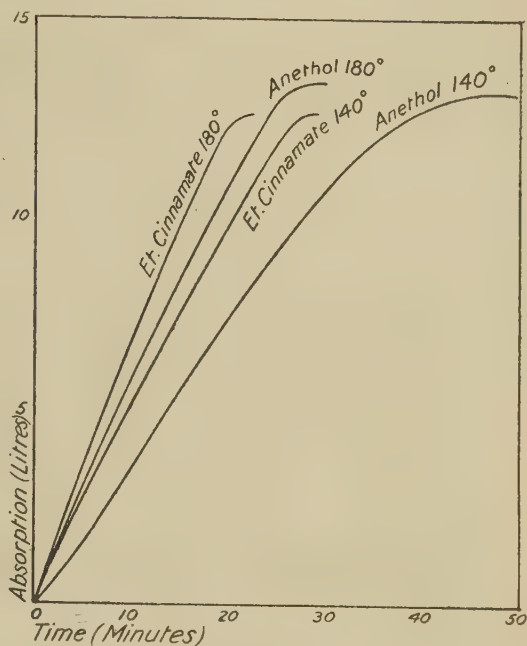


FIG. 2.

100 grm. Methyl Cinnamate and 0.15 grm. Nickel.

At 140°.

At 180°.

Hydrogen measured at 13.5°, V' = 14.50.				Hydrogen measured at 15.5°, V' = 14.60.			
<i>t</i> .	<i>v</i> .	$K = v/t$.	$K' = \frac{1}{t} \log \frac{V'}{V' - v}$.	<i>t</i> .	<i>v</i> .	$K = v/t$.	$K' = \frac{1}{t} \log \frac{V'}{V' - v}$.
3.0	1.00	0.333	0.0104	2.8	1.90	0.679	0.0216
6.4	2.15	0.336	0.0109	6.0	4.10	0.683	0.0239
9.7	3.20	0.330	0.0111	9.2	6.30	0.685	0.0266
12.8	4.20	0.328	0.0116	12.4	8.40	0.678	0.0300
15.9	5.20	0.327	0.0121	15.3	10.15	0.664	0.0337
19.0	6.10	0.321	0.0125	18.2	11.60	0.637	0.0378
22.1	7.00	0.317	0.0130	21.0	12.75	0.607	0.0427
25.2	7.90	0.314	0.0136	23.9	13.45	0.563	0.0462
28.4	8.65	0.305	0.0135	26.8	13.90	0.519	0.0492
31.5	9.50	0.302	0.0147	29.7	14.15	0.476	0.0509
34.6	10.15	0.294	0.0151	32.7	14.30	0.437	0.0516
37.6	10.70	0.285	0.0155	35.6	14.40	0.405	0.0523
40.5	11.20	0.277	0.0159				
43.5	11.60	0.267	0.0161				
46.4	12.00	0.259	0.0165				
49.3	12.35	0.251	0.0168				
52.3	12.60	0.241	0.0170				
55.3	12.85	0.232	0.0171				
58.3	13.00	0.223	0.0169				
61.3	13.15	0.216	0.0169				

A comparison between that part of the action over which the relation $K = v/t$ holds within the limits of experimental error and the duration of the whole process is afforded in the next table:—

Unsaturated compound.	Temperature.	Total hydrogenation.		Linear portion of graph.	
		Litres H_2 .	Absorbed in mins.	Litres H_2 .	Absorbed in mins.
	°				
Methyl cinnamate	140	13·15	61·3	7·90	25·2
Methyl cinnamate	180	14·40	35·6	10·15	15·3
Ethyl cinnamate	140	12·55	29·7	11·25	23·4
Ethyl cinnamate	180	12·55	22·4	10·25	15·9
Anethol	140	13·15	49·9	10·40	29·1
Anethol	180	13·40	30·3	10·10	18·6
Safrol	140	14·05	45·7	10·00	24·0
Safrol	180	13·05	29·5	9·55	17·6

Transformation from Linear to Logarithmic Curve in Presence of a Substance which can combine with the Catalyst.

In the hydrolysis of glucosides the hexose produced associates with the enzyme and has the effect of diminishing the active mass of the latter; on the other hand, at the temperature at which reduction is effected, the saturated product of hydrogenation has much less affinity for the catalyst than the unsaturated material, so that its effect in changing the character of the curve representing chemical action against time does not become evident till much later. An analogy to the withdrawal of the enzyme from hydrolytic activity is, however, to be found in the action on nickel of some feebly acidic compounds: these show the usual "poisoning" effect on the catalyst and in suitably chosen instances the rate of "poisoning" is sufficiently slow to make it comparable with the rate of hydrogenation. Under such circumstances the graph becomes a representation throughout of an approximately logarithmic action, the action measured in this case being essentially that of the decrease in activity of the catalyst. Thus, if isoeugenol or coumarin are hydrogenated, the curves are logarithmic as compared with the mainly linear graphs for anethol and safrol or the cinnamic esters. The difference between the different compounds is that isoeugenol is a phenol

$(CH_3O)(HO)C_6H_3.CH:CH.CH_3$, whilst coumarin, $C_6H_4 \begin{matrix} CH:CH \\ \diagdown \quad | \\ O-CO \end{matrix}$, is liable to

be transformed, in presence of traces of water, into *o*-hydroxycinnamic acid; also, in both cases, the product of hydrogenation is dark-coloured and contains certain decomposition products which do not appear in the other examples.

The curves for isoeugenol at 140° and 180°, and for coumarin at 180°, are given in fig. 3; the corresponding numerical data are as follows :—

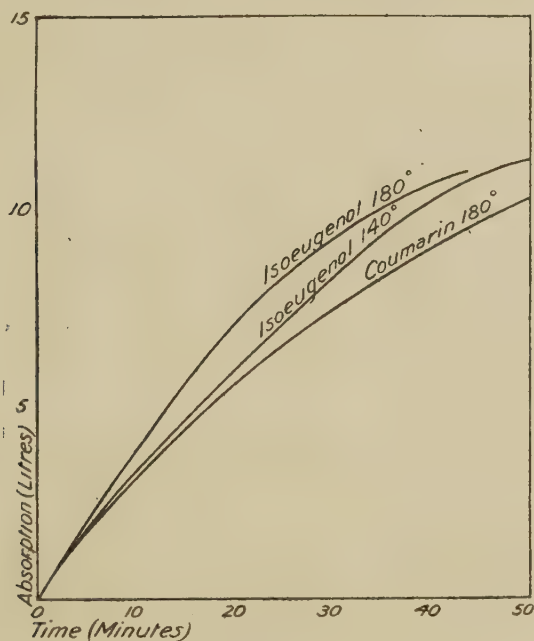


FIG. 3.

100 grm. Isoeugenol and 0.15 grm. Nickel.

At 140°.

At 180°.

Hydrogen measured at 19° ($V' = 14.60$).				Hydrogen measured at 19° ($V' = 14.60$).			
t .	v .	$K = v/t$.	$K' = \frac{1}{t} \log \frac{V'}{V' - v}$.	t .	v .	$K = v/t$.	$K' = \frac{1}{t} \log \frac{V'}{V' - v}$.
5.6	1.90	0.339	0.0108	6.0	2.30	0.383	0.0124
11.4	3.65	0.320	0.0109	12.2	4.60	0.377	0.0135
17.4	5.05	0.290	0.0106	18.5	6.60	0.357	0.0141
23.4	6.70	0.286	0.0114	24.8	8.25	0.333	0.0146
29.4	8.10	0.276	0.0119	31.1	9.50	0.305	0.0147
35.4	9.45	0.267	0.0128	37.5	10.40	0.277	0.0144
41.5	10.50	0.253	0.0133	44.0	10.95	0.249	0.0137
47.7	11.20	0.235	0.0133				
53.0	11.35	0.214	0.0123				

100 grm. Coumarin and 0.15 grm. Nickel.

At 180°.

Hydrogen measured at 20° ($V' = 16.45$).			
t .	v .	$K = v/t$.	$K' = \frac{1}{t} \log \frac{V'}{V' - v}$.
5.8	1.95	0.336	0.0094
12.0	3.65	0.304	0.0091
18.3	5.35	0.292	0.0093
24.6	6.45	0.262	0.0088
31.0	7.60	0.245	0.0087
37.4	8.65	0.231	0.0087
43.4	9.50	0.219	0.0086
48.8	10.20	0.209	0.0086
54.2	10.75	0.198	0.0085
59.7	11.20	0.188	0.0083

Transformation from Linear to Logarithmic Curves in the Hydrogenation of a Pure (Non-toxic) Compound, owing to Altering Concentration of Hydrogen.

If, instead of following our regular procedure of passing a constant stream of hydrogen through the open apparatus, it was converted into a closed system by sealing the inlet tube and connecting the exit to the hydrogen supply, so that any gaseous impurities accumulated in the gas-space above the liquid (except in so far as they might diffuse back against the incoming current of hydrogen), very consistent logarithmic curves were always obtained.

Some experiments made with ethyl cinnamate at 180° in the closed apparatus may be quoted: the hydrogen was dried over a long layer of anhydrous calcium chloride, and then passed through a narrow capillary about 75 cm. in length (to prevent any back diffusion), immediately before reaching the hydrogenation vessel. It was found that the rate of action observed was not in any way connected with the hydrogenation itself, but was simply a measure of the rate at which the free gas-space in the vessel was becoming filled with gaseous impurities.

The concentration of hydrogen in the free gas-space falls off as gas is absorbed in the action, and, if the rate of hydrogenation depends upon this concentration, and V'' is the total volume of hydrogen which could be absorbed before the free gas-space is completely filled with gaseous impurity, then it has been shown* that the measured rate of action is given by

$$\frac{dv}{dt} = K''(V'' - v),$$

or

$$K'' = \frac{1}{t} \log \frac{V''}{V'' - v}.$$

* 'Journ. Soc. Chem. Ind.,' vol. 39, p. 120, T (1919).

The value of V'' was determined in each experiment after analysis of the gas remaining in the free space above the liquid at the conclusion of the process. From the percentage of hydrogen (p) thus obtained, and the known total absorption of hydrogen, the percentage of hydrogen (P) in the original gas employed was calculated, and, from this, the volume of the gas-space having also been measured, the value of V'' was derived.

It may be remarked, in passing, that if a material could be found for hydrogenation which did not give up traces of gaseous impurities such as carbon dioxide or hydrocarbons, this process would form the basis of an exceedingly accurate method of hydrogen analysis, the explosion or combustion of the hydrogen being effected on a very small proportion of the total hydrogen (for example, in most of our experiments, the total absorption of hydrogen was about 12 litres, that remaining in the gas-space of the vessel being about 0.2–0.3 litres).

The results obtained with ethyl cinnamate at 180°C ., and three different

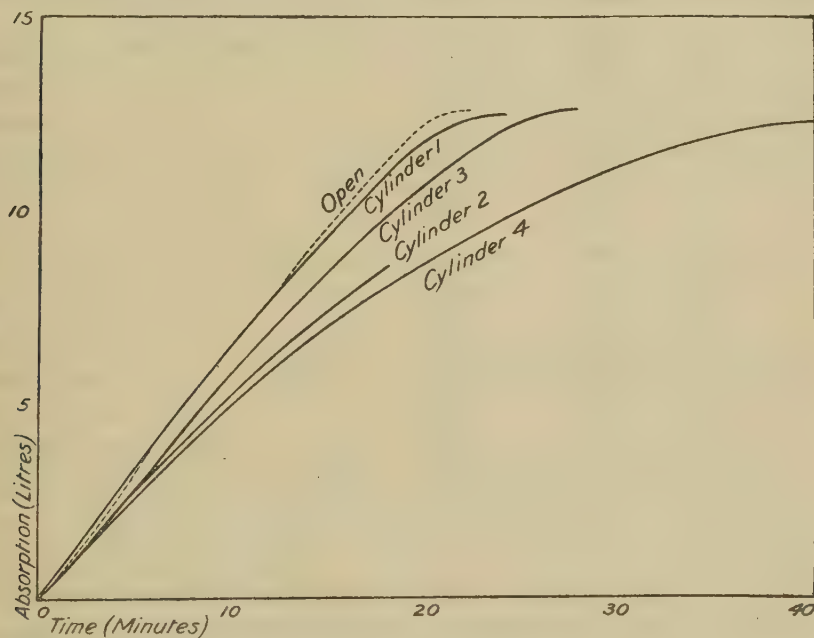


FIG. 4.

cylinders of electrolytic hydrogen, varying slightly in purity, are shown in the next Table, and graphically in fig. 4; in the Table are given

t , v , and $K = v/t$ as before.

K' the "unimolecular constant" calculated with respect to the total hydrogen absorbable by the ethyl cinnamate ($V' = 13.40$ at 15°),

p , P , and V'' as above,

and

K'' the "unimolecular constant" calculated with respect to the total hydrogen absorbable when the accumulated impurities would occupy 648 c.c. at 180° or 412 c.c. at 15° (the volume of the free gas-space in these experiments).

Cylinder.	t .	v .	$K = v/t$.	$K' = \frac{1}{t} \log \frac{V'}{V' - v}$.	p .	P .	V'' .	$K'' = \frac{1}{t} \log \frac{V''}{V'' - v}$.
No. 1	2	1.50	0.750	0.0258	75.8	99.21	51.78	0.0064
	4	2.78	0.695	0.0253				0.0060
	6	4.13	0.688	0.0267				0.0060
	8	5.33	0.666	0.0275				0.0059
	10	6.62	0.662	0.0296				0.0060
	12	7.80	0.650	0.0315				0.0059
	14	9.00	0.643	0.0345				0.0059
	16	10.03	0.627	0.0375				0.0059
	18	11.01	0.612	0.0416				0.0058
	20	11.89	0.595	0.0474				0.0057
	22	12.39	0.563	0.0510				0.0054
	24	12.47	0.520	0.0483				0.0050
No. 2	2	0.94	0.470	0.0158	65.1	98.47	26.52	0.0078
	4	2.25	0.562	0.0200				0.0096
	6	3.36	0.560	0.0209				0.0098
	8	4.36	0.545	0.0214				0.0097
	10	5.28	0.528	0.0218				0.0096
	12	6.20	0.517	0.0225				0.0096
	14	7.10	0.507	0.0234				0.0097
	16	7.90	0.494	0.0242				0.0096
	18	8.67	0.482	0.0251				0.0096
No. 4	2	0.89	0.445	0.0150	36.6	97.89	19.11	0.0103
	4	2.13	0.532	0.0188				0.0128
	6	3.24	0.540	0.0200				0.0134
	10	5.08	0.508	0.0207				0.0134
	12	5.94	0.495	0.0211				0.0135
	14	6.78	0.483	0.0218				0.0135
	16	7.43	0.464	0.0219				0.0134
	18	8.15	0.453	0.0226				0.0134
	20	8.78	0.439	0.0231				0.0134
	25	10.07	0.403	0.0242				0.0130
	32	11.45	0.358	0.0262				0.0124
	40	12.27	0.307	0.0268				0.0112

It is to be observed that

(i) With increasing purity of hydrogen, the ratio v/t approaches the constancy characteristic of hydrogenation in a continuous stream of hydrogen;

(ii) The values of K' increase throughout, but become more nearly concordant as the hydrogen purity decreases (they would, of course, be constant for $V'' = 13.40$ or $P = 97.0$ per cent.);

(iii) As the purity of the hydrogen and the speed of the action (measured by v/t) increase, the absolute values of the constants K'' fall; that is, the rate at which the gas-space becomes filled with impurity is smaller, the purer the hydrogen.

It is also to be borne in mind that this effect—the constancy of K'' —could not appear unless the actual hydrogenating action were (within the limit of experimental error), a linear function of the time. We have in common with other workers, found that substances such as fatty oils (under conditions which, in our “open” system of working, do not lead to a linear graph) do not give constant values for K'' in the “closed” system; on the other hand, if attention is confined to a well-marked linear portion of the curve obtained in the “open” system (such as the initial portion of the linseed oil curve, fig. 1), then when hydrogenating under the “closed” system over the same range of unsaturation, concordant values of K'' are found.

The bearing of this section on the enzyme experiments may be briefly considered; the corresponding pairs of interactants are nickel and enzyme, unsaturated compound and glucoside, and hydrogen and water.

The progressive alteration in concentration of the hydrogen therefore corresponds to circumstances in which the active mass of the water is varied; and although the analogy is perhaps not very exact, the result is similar to the competition between water and glucoside for an acid when an acid is used, in place of an enzyme as hydrolytic agent. One of us and R. J. Caldwell* have shown that this withdrawal of water by the acid, when the latter is present in more than very dilute solution, tends to suppression of the linear phase of hydrolysis.

When $v/t = K$ the Action is Independent of the Concentration of the Catalyst.

The relation $K = v/t$ implies that the amount of unsaturated compound present, and therefore its relation to the amount of catalyst present, has no influence on the action.

In other words, the amount of action is dependent only on the total mass of the catalyst present in the system, so that liquid hydrogenation and vapour catalyses such as hydrogenation, dehydrogenation, or dehydration are identical from this standpoint.

In practice, as we have pointed out, the relation $K = v/t$ cannot hold throughout the process, but in the case of liquid hydrogenation does so for a considerable range.

We have made some experiments on these lines on the hydrogenation of linseed oil; this material gives an initial linear portion of about 30 per cent. of the whole curve, corresponding to hydrogenation of all the linolenin and most of the linolein. A very abrupt curvature then sets in, and thereafter approximate linearity at much lower slope is resumed.

* ‘Roy. Soc. Proc.’ vol. 73, p. 534 (1904).

We examined varying weights of oil—200, 300, and 400 grm.—in each case with two weights of nickel, 1.50 and 0.45 grm. The resulting curves

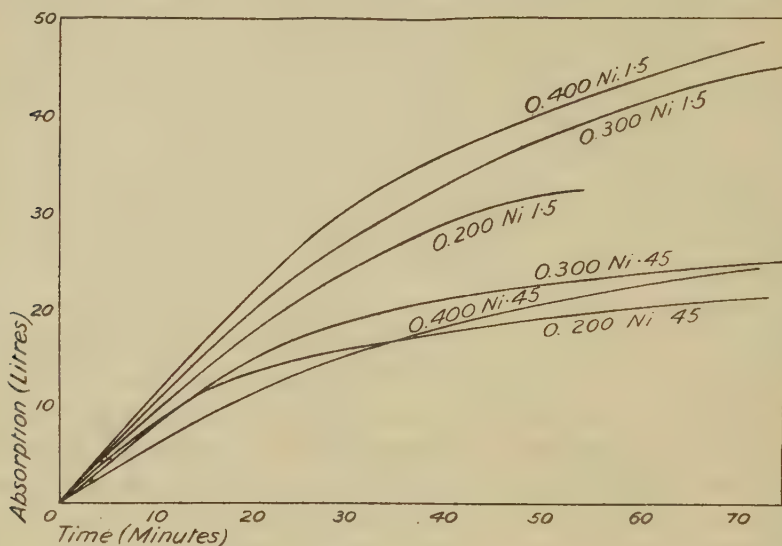


FIG. 5.

are shown in fig. 5, and the numerical data may be briefly summarised as follows:—

Linseed oil.	Nickel.	Hydrogenation curve.							Second approximate linear portion.		
		First linear portion.			Curvature.						
		<i>t.</i>	<i>v.</i>	<i>v/t.</i>	<i>t.</i>	<i>v.</i>	(<i>v/t.</i>)	<i>t.</i>	<i>v.</i>	<i>v/t.</i>	
200	1.5	12.3	11.95	0.971	10.4	7.85	(0.755)	18.7	10.15	0.543	
300	1.5	18.4	18.80	1.022	14.7	10.55	(0.718)	28.4	12.80	0.451	
400	1.5	23.4	25.25	1.079	16.6	10.85	(0.654)	32.2	11.90	0.370	
200	0.45	12.8	10.45	0.817	14.7	5.20	(0.354)	45.3	6.05	0.134	
300	0.45	16.0	12.65	0.791	16.5	7.20	(0.436)	41.2	5.50	0.133	
400	0.45	13.9	8.40	0.604	remainder curved throughout				abnormally.		

Three component factors are clearly visible:—

- (i) The dependence of the value of v/t on the mass of nickel present;
- (ii) The influence of impurities in the oil gradually affecting the catalyst;
and
- (iii) The load of oil in the apparatus.

With the larger amount of nickel, the rate of hydrogen absorption over the

first linear portion of the curve is very nearly constant whether 200, 300 or 400 grm. of oil are present, but it increases slightly owing to the fact that the mixing device employed tends to work more efficiently under full load.

On the other hand, with less nickel present, the rates are again nearly constant for loads of oil of 200 and 300 grm., but in the latter case the extra amount of impurity present in the increased quantity of oil commences to have a perceptible effect; with 400 grm. this effect is so marked that, after a much shortened linear portion, permanent curvature sets in, on account of the progressive depreciation of the catalyst and independently of the normal curvature of the hydrogenation progress itself.

Some General Considerations of Chemical Action at Solid (Catalytic) Surfaces.

The hydrolytic actions formerly studied by one of us and the actions of hydrogenation and dehydrogenation which have formed the subject of the present communications have proved equally open to explanation by processes of an essentially chemical character. Indeed, all our work has served merely to develop, on somewhat novel lines, the old view, first put forward by de la Rive and Marcet* that catalytic change is effected by the intermediate formation of definite chemical compounds; although we do not postulate in general the formation of intermediate compounds† of well-defined stability.

Indeed, it is our opinion that these are not to be expected in the course of catalytic change, the specific action of various catalysts probably depending largely on the suitable *instability* of the intermediate complex for the purposes of the action. In other words, change of the compounds which we have studied depends on the coincidence that the catalyst and the initial substance will interact to form a compound sufficiently unstable under the conditions prevailing to decompose (or interact with other constituents of the system) giving the new products.

* 'Ann. Chim. Phys.,' (2), vol. 39, p. 328 (1828).

† The physico-chemical data from which our present deductions are made do not afford any evidence as to the precise stoichiometrical relation subsisting between catalyst and organic compound. The latter is not necessarily simple, for example, an atom of nickel in temporary union with an organic group containing one ethylenic-linkage: it may be more probably of the nature of a "co-ordinated" compound (comparable to nickel carbonyl) in which the "subsidiary valencies" of the interactants play the chief part; or again, the combination might be still less definite and analogous to the adsorption of dyes by fibres, in which case the composition of the unstable complex might vary with physical conditions such as temperature or concentration. By "intermediate compound" in the present series of papers we mean an association between catalyst and the other components due to the same "chemical" forces which operate in more ordinary chemical actions, but we are not able to offer any opinion as to the precise character of the compounds thus transiently produced.

Owing to the influence of Ostwald, Nernst, and the late XIXth-century school of German physical chemists, the chemical view due originally to the above French scientists has been under a cloud, the first-named in particular refusing to accept a theory which could not give in every case definite proof of the existence of each intermediate compound cited, ascribing catalysis at solid surfaces to adsorption or physical concentration of the interactants at the surface, and advancing a series of dogmatic "criteria" of catalysis.

It is to be remembered, however, that the chemist and the physicist regard the question from different points of view, and that ultimately the physical and chemical explanations of catalysis must be found to be complementary and not antagonistic.

Lewis* has criticised some of Ostwald's "criteria," notably, that a catalyst cannot affect the final state of equilibrium, and is incapable of starting an interaction, and found them to be unsound. The physical disproof of these two articles of faith, which have for a long time conflicted with everyday experience of the worker on catalytic problems, is especially to be welcomed.

The phenomenon of adsorption was until lately regarded as a "diffusion layer," several molecules thick, of the adsorbed substance at the solid surface,† the rate of chemical interaction being a function of the rate of diffusion in this layer, and not depending on any actual chemical change at the surface of the catalyst.

More recently adsorption has been considered only to involve the formation of a single layer of molecules at a solid surface, the forces operating in holding atoms or molecules to such surface being "chemical" in nature, not purely physical. This view is generally associated with the work of Langmuir‡ but the idea of a molecular layer is in reality much older in origin.

Lord Rayleigh,§ we believe, was the first to draw attention to the fact that the operating film in the case of the reduction of the surface tension of water by olive oil is of the order of one molecule thick, his conclusions being confirmed by Devaux|| and Marcellin¶ and extended by W. B. Hardy.** The film begins to produce an effect with a layer one molecule thick; beyond this point the tension falls as the layer is thickened and there is a second critical point

* 'Trans. Chem. Soc.,' vol. 115, p. 1360 (1919).

† Cf. Bodenstein, 'Zeitsch. Physikal. Chem.,' vol. 29, p. 655 (1899); vol. 53, p. 166 (1905); Nernst, *ibid.*, vol. 47, p. 52 (1904).

‡ 'J. Amer. Chem. Soc.,' vol. 38, p. 2221 (1916); vol. 39, p. 1848 (1917); vol. 40 p. 1361 (1918).

§ 'Roy. Soc. Proc.,' vol. 47, p. 364 (1890).

|| 'Rev. gen. d. Sciences,' February, 1913.

¶ 'Ann. de Physique,' vol. 1, vol. 19 (1914).

** 'Roy. Soc. Proc.,' A, vol. 86, p. 631 (1912); vol. 88, p. 303 (1913).

where it is two molecules thick. Hardy has shown that the effect is determined by chemical constitution and increases with the reactivity of the substance.

It may be cited further that Lewis* has extended the radiation hypothesis, by which he explains many cases of "homogeneous" catalysis, to "heterogeneous" actions on the basis of the single layer adsorption theory.

Rideal† has shown that the rate of selective combustion of carbon monoxide when a mixture of carbon monoxide, hydrogen and oxygen is passed over a suitable catalyst agrees with "Langmuir's view" rather than with the earlier "diffusion" theory of Bodenstein.

It would seem, therefore, that the physical deduction that catalysis in heterogeneous systems is effected by adsorption of a single layer of the interactants at the solid catalytic surface (the adsorption being due to "chemical" forces) is indistinguishable from the chemical hypothesis of unstable intermediate compounds formed between catalyst and interactants, which has been forced by experimental facts upon the consideration of the chemist at intervals from 1828, when De la Rive and Marcet first suggested the idea, down to the present moment.

So far as we are concerned, we are convinced that the hypothesis of unstable intermediate compounds between the catalyst and interactants offers a reasonable explanation of the mechanism of all so-called "heterogeneous" catalytic actions and, in particular, of the following:—

- (i) Action of enzymes on sugar derivatives in aqueous solution, etc. ;
- (ii) The "Sabatier" catalyses of organic compounds in presence of finely divided metals or metallic oxides, including hydrogenation and dehydrogenation, hydration and dehydration, formation of ethers and ketones, the specific action of finely divided metals on the vapours of aliphatic acids, and the combined dehydration and condensation processes effected by certain metallic oxides leading to the production of ethers, amines, thiols, esters, etc., from alcohols or phenols ;
- (iii) The interaction of carbon monoxide and steam conditioned by various solid substances.

Actions of this type are produced in a system at first heterogeneous, but the actual interaction takes place in a homogeneous system composed of the solid catalyst and its associated compounds, and as such follows the law of mass action, proceeding at a constant rate so long as the acting mass of the catalyst is itself constant.

* 'Trans. Chem. Soc.,' vol. 115, p. 182 (1919).

† 'Trans. Chem. Soc.,' vol. 115, p. 993 (1919).

In conclusion, we claim to have established that, in the case of an active catalyst where the surface concentration of the adsorbed compound is at a maximum, chemical action takes place at a regular rate so long as an adequate supply of the interacting substances is maintained at the surface. The forces regulating this supply may be physical rather than chemical in nature.

The Origin of the "Cyanogen" Bands.

By S. BARRATT.

(Communicated by Prof. T. R. Merton, F.R.S. Received June 5, 1920.)

There are, in addition to the line and the positive and negative band spectra of nitrogen, several other series of bands, in the production of which this element plays some part. The emission centres responsible for these bands have generally been identified with the molecules of compounds of nitrogen with other elements, though these molecules are not necessarily those of compounds which can be isolated under normal circumstances, and possibly may prove to be more of the nature of temporary associations. Such spectra include the so-called third positive band spectrum of nitrogen, the various spectra attributed to ammonia or other nitrogen-oxygen complexes, and also the cyanogen bands.

The NO bands, Deslandres' third positive group of nitrogen bands, are found in vacuum tubes filled with nitrogen, when they contain a trace of oxygen as impurity. They have also been observed in the carbon arc surrounded by a magnesia block,* in uncondensed spark discharges in air and nitrogen, and in the flames of cyanogen and ammonia. They were formerly believed to be due to nitrogen alone, but Deslandres, Schniederjost, Lewis and others have proved that their production is dependent upon the presence of oxygen.

The spectra obtained from compounds or mixtures of nitrogen and hydrogen are more complex. What is probably the true ammonia spectrum was discovered by Schuster.† It was observed when a continuous stream of ammonia was passed through a vacuum tube, and disappeared immediately upon interruption of the gas flow, presumably owing to complete decomposition of the ammonia. Another spectrum is characterised by a strong

* Liveing and Dewar, 'Roy. Soc. Proc.,' vol. 34, p. 418 (1882).

† 'Roy. Soc. Proc.,' vol. 20, p. 484 (1872).

band in the ultra-violet, with a head at λ 3360. It was discovered by Eder* in the flame of ammonia burning in oxygen.

Lewis† observed the same band in vacuum tubes containing nitrogen and hydrogen, and found that the presence of both gases was essential for its production. The band has been observed in the carbon arc by King‡; and Fowler,§ who has succeeded in identifying this band in the solar spectrum, mentions its occurrence in the flame of wet cyanogen. Owing to the persistent appearance of the band in company with the cyanogen bands, it has frequently been confused with a part of the latter spectrum.||

The persistence of this band in vacuum tubes filled with ammonia, after the disappearance of Schuster's spectrum, and its presence in the solar spectrum, indicate that the centres responsible for the emission of the two spectra are different.

Judging from its conditions of stability, it is some compound of nitrogen and hydrogen other than ammonia which is responsible for the band at λ 3360, and, whilst referring to this band as the "ammonia band," Fowler expressly recognised that this possibility is not excluded.

The cyanogen bands were originally attributed to a compound of carbon and nitrogen, as they are characteristic of the flame of burning cyanogen, and of the carbon arc in nitrogen. Lockyer (1880) claimed that these bands were as strongly developed in the carbon arc burning in dry chlorine as in the ordinary arc in air. Later, also, he observed the bands when a spark discharge was passed through carbon tetrachloride vapour. He concluded that the bands were part of the Swan spectrum, nitrogen not being essential for their production. This theory was contested by Liveing and Dewar,¶ who found that the bands could not be developed under the conditions imposed by Lockyer, if the last traces of nitrogen were rigorously excluded, and showed, in fact, that the appearance of the bands was an exceedingly delicate test for the presence of nitrogen in any form.

Foley** observed that the intensity of the cyanogen bands from the carbon arc is by no means proportional to the amount of nitrogen present. He stated that the intensity of the bands from the arc in cyanogen is little greater than from that in air, and, further, that the intensity is not much diminished by replacing the air by carbon dioxide. He inclined to the

* 'Denkschr. Wien. Akad.,' vol. 60, p. 1 (1893).

† 'Astrophys. Journ.,' vol. 40, p. 154 (1914).

‡ 'Astrophys. Journ.,' vol. 14, p. 323 (1901).

§ 'Phil. Trans.,' A, vol. 218, p. 351 (1919).

|| Cf. King, *loc. cit.*, and Kayser, 'Handbuch der Spectroscopie,' vol. 5, p. 229.

¶ 'Roy. Soc. Proc.,' 1880.

** 'Phys. Rev.,' vol. 5, p. 149 (1897).

view that the cyanogen bands are due to carbon in the presence of nitrogen, but not combined with it.

It was generally conceded, however, that the bands only appeared under conditions ensuring the presence of both nitrogen and carbon, until the question was re-opened in 1914, by Grotrian and Runge.* Their conclusions, which have been widely accepted† were to the effect that the cyanogen bands were due to nitrogen alone.

The experimental basis for this statement was derived from a study of the conditions under which the spectrum may be observed in the Schonherr elongated arc. This type of discharge has some advantages over the ordinary arc for spectroscopic work. Grotrian and Runge claim that the spectra due to the electrode materials are only visible in the immediate neighbourhood of the electrodes themselves; all impurities, also, are swept away by the current of gas necessary to preserve the stability of the arc. If this be so, the spectrum emitted from the central part of the arc will depend only upon the nature of the gas passing through it. The cyanogen bands were found under these conditions, with nitrogen, prepared in the usual manner from liquid air, streaming through the arc. Their intensity was unaffected by the composition of the electrodes, for which copper, iron, platinum, magnesium, aluminium, and carbon were successively used. No other bands usually attributed to carbon were detected; and, finally, the intensity of the bands remained unaltered after the introduction of varying proportions of carbon dioxide. The conclusion drawn from these observations was that carbon is not essential for the production of the cyanogen bands. The absence of the bands from the spectra of metallic arcs in air, which would appear to militate against this view, Grotrian and Runge explained by an inhibiting effect of oxygen upon their development. Their appearance in the carbon arc was held to be due to the removal of the atmospheric oxygen as carbon oxides.

In illustration, they quote an experiment with an arc between copper electrodes. In nitrogen containing a little oxygen, this arc did not show the cyanogen bands, but these appeared when the nitrogen entering the chamber had previously been passed through pyrogallol.

Hemsalech, recently‡ stated in a footnote that as a result of his own experiments he was unable to endorse these views; and, indeed, added that he has obtained indications that the presence of nitrogen is not always essential for the emission of the bands.

* 'Phys. Zeitschr.,' vol. 15, p. 545.

+ Cf. Stähler, 'Handbuch der Arbeitsmethoden,' vol. 2, i, 497; and St. John 'Astrophys. Journ.,' vol. 46, p. 251 (1917).

‡ 'Phil. Mag.,' vol. 39, p. 256 (1920).

The experiments described in this paper originated with an observation of the peculiar appearance of the coal-gas nitrous oxide flame, which suggested the possibility of detecting a spectrum peculiar to the latter gas. Though no indications of a new spectrum were detected in the various flames examined, the results proved to be of some interest in relation to the origin of the cyanogen bands.

As a preliminary, the spectrum obtained by streaming nitrous oxide through a vacuum tube was studied, after the method introduced by Schuster for ammonia. The inlet of the vacuum tube was fused to a long and fine capillary, which regulated the rate of inflow of the gas; and the outlet of the tube was attached to a mechanically driven air-pump. The nitrous oxide was taken from a cylinder supplied for medical use. The green "after-glow" of the gases leaving the path of discharge was stronger in nitrous oxide than in air.

Photographs were taken of the discharges in the capillary of the vacuum tube when nitrous oxide and air, successively, were allowed to pass through the tube. No new bands appeared in the nitrous oxide discharge, but several bands, also visible with air, were considerably intensified with respect to the rest of the spectrum. These were measured by means of a comparison spectrum and included a diffuse band in the yellow, stretching from $\lambda = 5992$ to 5969 , and three bands of about $\lambda = 5517$, 5407 , and 5397 A.

The remaining observations were made upon the spectra of various flames. The burner used with these flames was a small brass hand blowpipe, of a type in which the gases were thoroughly mixed before reaching the jet. The axis of the flame was arranged vertically in front of the slit of the spectrograph, and the light was focussed upon the slit by a quartz lens. This arrangement permits the analysis of the light from the various cones of a flame. A Hilger quartz spectrograph was used, with a dispersion of 35 A. per millimetre at $\lambda = 4000$ A. It was provided with a wave-length scale which could be photographed on the plate, in juxtaposition to the flame spectrum, and which was of great assistance for the purpose of identification.

The nitrous oxide was taken direct from a cylinder, and as it was of the purity exacted for medical purposes, it was considered to require no further purification. The hydrogen was also taken from a cylinder, and the preparation of the other gases is described below.

Nitrous Oxide—Coal-Gas Flame.

The structure of this flame is complex, as it possesses at least five zones. The innermost, and brightest, is yellow and is brilliantly luminous at its apex. The greenish yellow mantle is common to all the flames obtained with

nitrous oxide and appears to be a general feature of all flames in air in which nitrogen compounds are burnt. In presence of a large proportion of nitrous oxide, just before the flame becomes unstable, the inner cones shrink into a single small cone, which is purple in tint. No new bands were found in the spectrum of the flame. The spectrum of the inner cone, photographed as has been described, contained the following groups:—

The Swan bands with heads at λ 5164, λ 4736, and λ 4381.

The CH bands with heads at λ 4315.

The OH bands with heads at λ 2811 and λ 3063.

The CN bands with heads at λ 4600, λ 4216, λ 3883, and λ 3590.

The NH band with a head at λ 3360.

The hydrocarbon bands (Eder's $C\eta$ band)* from λ 4048 to λ 3872.

All these were strongly developed.

Nitrous Oxide—Hydrogen Flame.

The strong development of the cyanogen bands in the nitrous oxide coal-gas flame suggested a method by which Grotrian and Runge's conclusions as to the origin of the cyanogen bands might be put to the test. If the bands are emitted by nitrogen, as they claim, independently of the presence of carbon (except as a reducing agent, as in the carbon arc), then the appearance of the bands in the flame just described must be attributed to the nitrous oxide alone, and should be unaffected by the substitution of hydrogen for the coal-gas as a constituent of the flame. The nitrous oxide-hydrogen flame was accordingly photographed. In structure the flame resembles that obtained with coal-gas, but its spectrum is more simple. The water vapour and the "ammonia" bands were very strong, but the Swan spectrum, the CH band, and the bands attributed to hydrocarbons were all absent. As the cyanogen bands in the first photograph taken were practically as intense as they had been in the coal-gas flame, it was thought that confirmation of Grotrian and Runge's theory had been obtained. Eventually, however, the appearance of the bands was traced to the use of rubber gas connections which had been employed in the experiments with coal-gas. When these were replaced by fresh pieces of tubing which had been treated for some time with boiling water, the photograph showed only a trace of the cyanogen head at λ 3883, and this was so weak that it could only be detected on very close examination of the plate. The intensity of the "ammonia" band, on the other hand, was unaffected.

In a subsequent experiment it was found possible, by further precautions, to obtain a plate showing no trace of the cyanogen bands. The burner was

* Eder and Valenta, 'Denkschr. Wien Akad.,' vol. 67, p. 483 (1899).

thoroughly cleaned with acid, and steam was blown through it for a considerable time. The length of rubber tubing actually coming into contact with the gases was reduced to a minimum, and, as a further precaution, both gases were passed through long glass tubes packed with solid caustic soda, to remove carbon dioxide. Under these conditions the last trace of the head at λ 3883 disappeared, though a slightly longer exposure was given than in the previous experiments. It would thus appear that atmospheric carbon dioxide is unable to cause the production of the cyanogen bands in the inner cone of such a flame. Both the band at λ 3360 and the water vapour bands were present with unaltered intensity. These observations appear to leave no doubt that the presence of carbon is essential for the emission of the cyanogen bands in flames. If the bands were due to nitrogen, the introduction of the volume of hydrocarbon that could escape from a short length of rubber tubing, after passage of a considerable volume of hydrogen beforehand, should not have affected appreciably their intensity. Actually the presence of this trace of hydrocarbon resulted in the strong development of all the cyanogen bands; while, when the contaminated tubing was removed, the head of the strongest band could barely be detected, and when further precautions were taken to ensure the elimination of carbon, even this persistent head at λ 3883 also disappeared.

It is evident that the cyanogen bands constitute a more delicate test for the presence of carbon in flames than do the remaining carbon bands, and that the cyanogen band at λ 3883 persists in the presence of extremely minute quantities of carbon.

Carbon Monoxide—Nitrous Oxide Flame.

This flame was thought to be worth investigating, as it contains no hydrogen. If the origin of the "ammonia" band is a nitrogen-hydrogen molecule, its production should not be possible when the presence of hydrogen in the burning gases is excluded. The carbon monoxide was prepared by the action of concentrated sulphuric acid upon formic acid. It was stored over dilute alkali, and was passed, previous to combustion, over solid caustic soda, soda lime, and calcium chloride. The flame resembles in structure that of carbon monoxide burning alone in air, but is white, instead of having the familiar blue colour. It has the usual yellow-green mantle, which has been mentioned above. The spectrum contained only the "continuous" band of burning carbon monoxide with, faintly superimposed upon it, the water vapour bands at λ 2811 and λ 3063. There was no indication of either the cyanogen, or the "ammonia" bands. The absence of the latter band is confirmatory evidence for the view that the presence of hydrogen is essential for its

emission. The appearance of the OH bands is to be attributed to atmospheric water vapour.

Carbon Monoxide—Nitric Oxide Flame.

This flame was examined in order to confirm the observations made with the corresponding nitrous oxide flame. The nitric oxide was prepared in the usual manner from a mixture of sodium nitrate and ferrous sulphate, by the action of concentrated sulphuric acid.

The appearance and spectra of the two flames were identical, and the cyanogen bands and the "ammonia" bands were again absent.

The absence of the cyanogen bands from both these flames is interesting. The fact that they were not developed appears to indicate that the chemical reactions in these flames are unfavourable to the production of the carbon-nitrogen compound responsible for the cyanogen bands, a circumstance which is not *a priori* improbable, when it is borne in mind that the carbon present is already partially oxidised, and would tend to pass into carbon dioxide directly in the process of combustion.

Carbon Monoxide—Ammonia Flame.

The absence of the cyanogen bands from the CO—N₂O, and CO—NO flames suggested the examination of a carbon monoxide flame fed with ammonia, in place of an oxide of nitrogen; for in this case the reducing action of the ammonia on the carbon monoxide might reasonably be expected to favour the probability of the formation of cyanogen. The carbon monoxide was charged with ammonia before reaching the jet by passage over the surface of a concentrated aqueous solution of ammonia. The flame presented the characteristic yellow coloration of flames which contain ammonia, and the water vapour and the ammonia band at λ 3360 were well developed, while the cyanogen band at λ 3883 was faintly visible. The "continuous" carbon monoxide spectrum was also present.

This broad band of burning carbon monoxide has generally been considered truly continuous, but in all the photographs obtained during these experiments, it appeared to be distinctly banded. Between wave-lengths $\lambda = 5000\text{--}3000$ Å the spectrum was crossed by a large number of diffuse bands, at an average interval of about 20 Å. These were unfortunately not sufficiently well differentiated from the continuous background for accurate measurements to be made. It is improbable that their presence can be traced to any impurity in the gases employed; and they were also observed in the flame of carbon monoxide burning alone in air.

Oxy Coal Gas Flame.

The explosion region of this flame exhibits only the $\lambda 3883$ head of the whole cyanogen spectrum, and that extremely faintly, though the hydrocarbon band $C\eta$, with heads at $\lambda 3872$ and $\lambda 3893$, is strongly developed. The "ammonia" head at $\lambda 3360$ is quite distinct, being much stronger than the cyanogen head. The appearance of these two heads may almost certainly be attributed to the traces of nitrogen compounds inevitably present in coal-gas.

With a view to a further determination of the conditions affecting the development of the cyanogen bands, several nitrogen compounds were introduced in small quantity into the oxy-coal-gas flame, and the spectrum of the inner cone photographed. The compounds used were ammonia, nitroethane, and piperidine. The addition of each of these resulted in the appearance of the cyanogen bands at $\lambda 3883$ and $\lambda 3590$, quite strongly developed, while the "ammonia" band was also strengthened. These observations show that elementary nitrogen is probably inefficient in producing the cyanogen bands in the oxy-coal-gas flame, while any form of combined nitrogen is capable of producing them.

Conclusions.

1. In conjunction with previous existing evidence, the observations recorded above seem to leave no doubt that the production of the cyanogen bands is due to a carbon-nitrogen compound, and to neither element alone. A summary of the evidence available from the study of flame spectra is given.

Flames in which CN bands are developed.

1. Coal-gas-nitrous oxide.
2. Coal-gas-air (+ ammonia, nitroethane or piperidine).
3. Carbon monoxide-air and NH_3 .
4. $(CN)_2$ and HCN-air.
5. Methylamine-air, and in the flames of other nitrogenous organic substances.

Flames in which CN bands are absent.

1. Hydrogen-nitrous oxide.
2. Hydrocarbon-oxygen flames in general.
3. Ammonia-oxygen.
4. Carbon monoxide-oxides of nitrogen.

It will be seen that in no case are the bands developed unless both carbon and nitrogen are present in the flame. Perhaps the clearest demonstration that carbon plays an essential part in the emission of these bands is afforded by the result of the addition of a trace of hydrocarbon to the nitrous oxide-hydrogen flame.

Evidence, from sources other than flame spectra, is not lacking. It is known, for example, that the cyanogen bands are not developed in vacuum tubes containing pure nitrogen and hydrogen, while the addition of traces of hydrocarbons, or of other carbon compounds, causes their appearance. The

bands are one of the most conspicuous features of the carbon arc in air, but are either absent from or only faintly visible in metallic arcs. Grotrian and Runge's explanation, which is based on the reducing powers of carbon relative to those of the metals, is difficult to uphold in view of the absence of the bands from the magnesium arc in air. That they do sometimes appear faintly in such metallic arcs is only to be expected, when the extreme difficulty of obtaining samples of metals free from traces of carbon is borne in mind. There is no doubt that Grotrian and Runge are correct in their statement that the presence of oxygen is unfavourable to the production of the bands, a fact which accounts for their detection in metallic arcs in nitrogen, when oxygen is excluded. This does not prove, however, that the bands are produced independently of the presence of carbon.

The evidence, by which Grotrian and Runge support their conclusion that the cyanogen bands are due to nitrogen alone, rests upon two assumptions:—

(i) That the nitrogen may be considered to be free from carbon when the Swan and other carbon bands are absent.

(ii) That if the cyanogen bands were due to a carbon complex, their intensity would be proportional to the amount of carbon present.

The first assumption is definitely disproved by the possibility of adding sufficient carbon to the nitrous oxide-hydrogen flame to cause the strong development of the cyanogen bands, while the remaining carbon bands cannot be detected. Hemsalech (*loc. cit.*) made a parallel observation with regard to the spectrum of the "red fringe" developed under an electrically heated graphite plate. The cyanogen head at $\lambda 3883$ was detected when the plate was heated to 2500°C. , while the Swan bands only appeared at a temperature 500°C. higher.

It is clear that it is an easy matter to realise conditions under which the cyanogen bands can be developed independently of the rest of the carbon spectrum. The production of the cyanogen head at $\lambda 3883$ can, in fact, be made to yield the most delicate test for the presence of carbon.

This fact invalidates the conclusion drawn from Grotrian and Runge's demonstration of the inhibiting effect of oxygen on the appearance of the bands in the copper arc burning in nitrogen. The passage of the gas through pyrogallol (which was used as an oxygen absorbent), in the experiment they describe, might account for the development of the cyanogen bands, while the rest of the carbon bands would still remain invisible.

That the second assumption is also untenable without further experimental support was shown by the same observation with the nitrous oxide-hydrogen flame. The addition of a very small percentage of hydrocarbon to the hydrogen caused almost as intense a development of the bands

as did the complete replacement of hydrogen by coal-gas. Foley's observations (*loc. cit.*) are worth recalling in this connection. He found that the intensity of the cyanogen bands in the carbon arc bear little relation to the amount of nitrogen available. It may be noted also that Grotrian and Runge considered the "ammonia" band at λ 3360 to be part of the cyanogen spectrum; evidence based on a discussion of this band is obviously irrelevant.

Summary.

(i) Observations have been made of the spectra of the flames of a number of gases containing carbon, hydrogen, nitrogen, and oxygen.

(ii) The cyanogen bands are strongly developed in the coal-gas-nitrous oxide flame.

(iii) Evidence has been obtained that they are entirely absent from the hydrogen-nitrous oxide flame, if all traces of carbon are excluded, and it appears to follow that the presence of carbon is essential to their production.

(iv) The appearance of the cyanogen bands is, under appropriate conditions, a more delicate test for carbon than that of any of the other bands associated with that element. On the other hand, this spectrum is not necessarily developed when both carbon and nitrogen are present.

(v) The conclusion of Grotrian and Runge, that the cyanogen spectrum is to be attributed to nitrogen, is shown to rest on assumptions which are not confirmed in the present investigation.

(vi) The cyanogen spectrum provides a very delicate test for the presence of compounds of nitrogen admitted in the form of a gas to hydrocarbon flames burning in air, since elementary nitrogen does not appear, under ordinary circumstances, to be effective in producing cyanogen bands in such flames.

(vii) The intensity of the cyanogen bands, when carbon compounds are admitted to the hydrogen-nitrous oxide flame, bears no simple relation to the amount of carbon thus added.

The subject of this communication was suggested to me by Prof. T. R. Merton, and the experiments were carried out in his laboratory. I wish to express my gratitude for the constant interest he has taken in the work, and for the help he has given me during its progress.

Moving Striations in Neon and Helium.

By F. W. ASTON, M.A., D.Sc., and T. KIKUCHI.

(Communicated by Prof. Sir E. Rutherford, F.R.S. Received June 23, 1920.)

During some work on Neon Lamps for Stroboscopic Work,* it was noticed that, when the flash of an ordinary spectrum tube containing neon was analysed by a rotating mirror, it consisted of two parts, an extremely short flash followed by a flame or arc, and that the latter consisted of bright striations travelling from anode to cathode. The same phenomenon was observed with helium. The velocity of these striations was roughly measured, and found to be about 50,000 cm./sec. in neon and 100,000 cm./sec. in helium. As these figures approximated to the velocities of sound in these gases, it was hoped that investigation of the phenomenon might lead to an explanation of striations generally. This expectation has, unfortunately, not been realised, for these velocities were soon found to be special or limiting cases of far more complex phenomena. The following paper is an account of the preliminary experiments, which have given interesting, but somewhat inconclusive results.

The first account of moving striations observed by means of a rotating mirror is given by A. Wüllner.† They were investigated more fully by W. Spottiswoode.‡ Both these observers used several elementary gases then available, but most of Spottiswoode's results were obtained with compounds, these giving more definite striations. Unfortunately, neither observer recorded any figures for the velocities, but Wüllner mentions that his mirror was rotated at $\frac{1}{2}$ to 2 revolutions per second.

Apparatus and Method.

The discharge tubes employed were of several different lengths and diameters; they were mounted horizontally and connected with a pump, charcoal-liquid air tube, and manometer, in such a way that pure gas could be introduced and its pressure measured.

The rotating mirror was mounted on the shaft of a small motor about two metres distant from the tubes, with its axis of rotation horizontal. On the same shaft was fixed the circuit breaker of the induction coil, so that the flashes were synchronised with the rotation of the mirror. The speed of rotation was read off by means of a revolution indicator.

* 'Proc. Camb. Phil. Soc.,' vol. 19, p. 300.

† 'Pogg. Ann.,' Jubelband, p. 32 (1874).

‡ 'Roy. Soc. Proc.,' vol. 25, p. 73 (1876).

When the coil was in operation, the appearance was somewhat as indicated in the sketch (fig. 1), the striated discharge being seen as a series of wavy streaks alternately dark and bright. It is clear that, if we know the rate of rotation of the mirror and its distance from the tube, the velocity of the striations may be measured by the slope of the bright streaks.

The first method used was to employ a fixed cross-wire at about 45° and vary the speed of the motor until the striations were parallel to this. Later, it was found more convenient to keep the speed constant and use a movable cross-wire, the angle of which was measured. This could be done to about half a degree, which was amply accurate for the work at this stage, for the velocity was very unsteady even in the same tube under apparently constant conditions.

Experiments with Neon.

Preliminary experiments were done on three spectrum tubes containing this gas, one being the tube with which the effect was first observed. The general appearance of the discharge was as indicated in fig. 1. As already mentioned, it consists of two distinct parts: first, a practically instantaneous flash, shown as a line, then the striated discharge, which is of considerable duration. The wavy appearance of the sloping lines indicated considerable variation in velocity, but in the case of fine tubes the mean angle of slope could be determined with fair accuracy. Alterations in the intensity of the spark, by increasing the current through the primary of the coil, made no noticeable change in the mean velocity of the striations. This may be due to the fact that the duration rather than the current density of the discharge is affected by this.

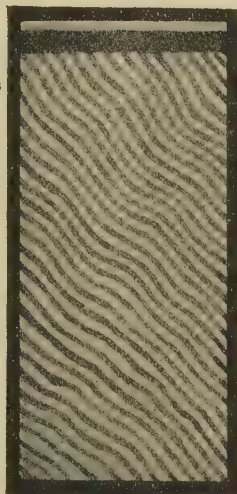


FIG. 1.

The following values for the velocity were obtained on the first trial:—

Original tube, diameter about 1.5 mm., pressure low	5.02×10^4 cm./sec.
Quartz tube filled with very pure neon	5.21×10^4 „
Narrow bore small tube	5.76×10^4 „
Original tube refilled at a higher pressure	2.89×10^4 „
Another tube refilled at a higher pressure	3.49×10^4 „

From these results it was evident that the mean velocity was not a constant, but appeared to depend on the pressure of the gas and the width of the bore.

Effect of Change of Pressure.

The first experiments on this were performed with three tubes having a capillary part 8-9 cm. long; their diameters were: Tube 4, 0.568 mm.; Tube 5, 1.41 mm.; and Tube 6, 1.874 mm. respectively. Neon of the highest purity was used and the pressure varied from a low value to 111 mm. Hg. No striations were visible at pressures less than 1 mm. in any of the tubes. Above 2 mm. Tubes 5 and 6 showed them, but not very distinctly; above 5 mm. striations could be seen in the narrowest tube. As the pressure is increased, they become more distinct and wider apart, but fluctuations in velocity become greater and there appears to be a general change in velocity towards the finish of the flash. The most striking effects are exhibited at about 10 mm. pressure; above this there is a tendency for the pattern to become closer, but even up to 111 mm. pressure the striations are clearly visible.

Results of velocity measurements are plotted in fig. 2. They are very

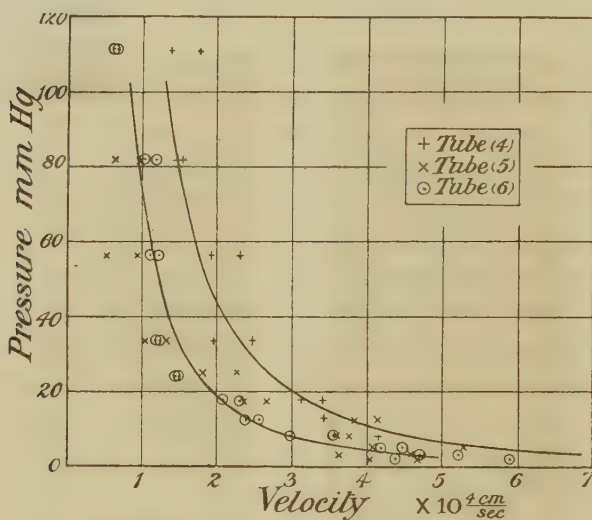


FIG. 2.

irregular, as the quantity measured was subject to wide fluctuations. The general result is that the velocity is very roughly proportional to the inverse square root of the pressure and is greater the narrower the tube. The following are the mean values if the pressure is expressed in millimetres of mercury:—

Tube 0.568 mm. diameter	$13.4 \times p^{-\frac{1}{2}} \times 10^4$ cm./sec.
Tube 1.41 mm. diameter	$8.6 \times p^{-\frac{1}{2}} \times 10^4$ „
Tube 1.87 mm. diameter	$8.5 \times p^{-\frac{1}{2}} \times 10^4$ „

The velocity appears to depend on the purity of the gas; a small quantity of impurity, probably hydrogen, increases the velocity of the striations and at the same time decreases the range of pressure over which they can be observed. If the quantity of impurity becomes at all large, the striations cannot be seen at all.

Experiments with Wide Tubes.

Tubes of much wider diameter, 7 mm. and 16 mm. were tried, one of the latter being 40 cm. long. In these tubes when the fresh gas was admitted, the colour of the discharge was bluish, and showed the mercury lines strongly in the spectroscope. When liquid air was applied to a side tube these gradually disappeared, and the discharge became redder. Observed with the rotating mirror, moving striations were first seen of a bluish colour, close together and not very distinct. Later, as the mercury was removed, the striations became red, distinct, and further apart. Their movements gave a very curious pattern. Fig. 3 is a rough sketch of the effect in the 7 mm. tube at 10.5 mm. pressure. Fig. 4 shows that seen in the 16 mm. tube at



FIG. 3.

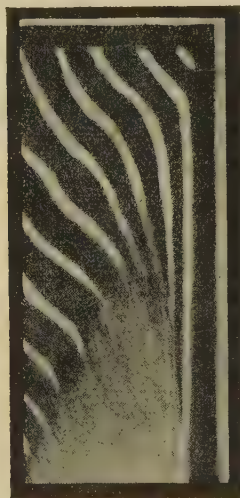


FIG. 4.

5 mm. pressure. The expression "mean velocity" has no longer any meaning, as the striations move from the anode end at velocities of about $1-2 \times 10^4$ cm./sec., but slow down at the cathode end. Some appear to develop into the stationary striations, which can be seen without the aid of the mirror. As the pressure is increased, the velocity at the anode end tends to become smaller, and with wider tubes the striations are further apart.

Effect of Condenser Discharge.

If a condenser is put in parallel with the tube, the first flash becomes very bright, but the succeeding striations are fainter. If the true condenser discharge (B spark) is employed, the first flash is exceedingly bright, but no striations are seen. With a static machine, the discharge appears as a series of bright instantaneous flashes only, but with a condenser and a very large resistance in the circuit, very faint moving striations were visible. Coating the discharge tube with earthed tinfoil did not appear to affect the discharge at all.

Effect of Change of Temperature.

In order to measure the effect of temperature change a tube 1.4 mm. diameter was mounted inside a metal jacket which could be heated. Measurements of velocity were made at constant pressure, others at constant volume. Fig. 5 indicates the curves obtained at a constant pressure of 11 mm. One of the curves represents the values obtained with the current in one direction, the other those with the current reversed. The difference in velocity is probably due to the tube ends and electrodes not being symmetrical. The part of the curves between A and B is probably the effect in pure neon; the temperature coefficient is 0.0011 to 0.0015 much less than the expansion coefficient of the gas 0.0037. The very rapid increase shown in the part BC appears to be due to traces of impurities liberated as the temperature is raised.

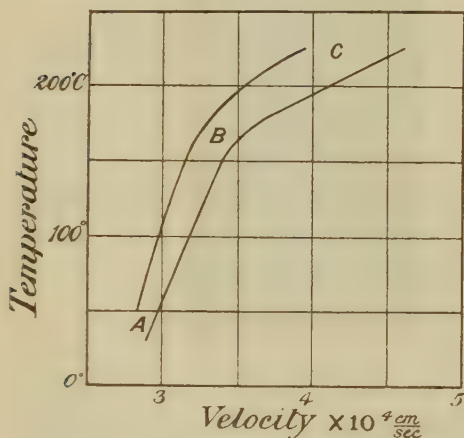


FIG. 5.

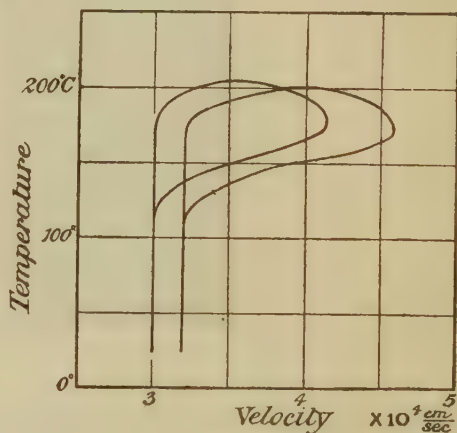


FIG. 6.

At constant volume (initial pressure 10.5 mm.) the velocity keeps practically constant up to 170° C. when it rapidly increases as shown by the curves in fig. 6. If the tube is allowed to cool a loop is formed. This is exactly the effect to be expected if a small quantity of impurity was liberated from the glass walls and then re-absorbed on cooling.

Temperature Effect in Presence of Mercury.

When liquid mercury is introduced into a tube containing neon and its temperature gradually raised, at constant volume, the striations steadily decrease in velocity until they are no longer visible. The results shown in fig. 7 were obtained with a tube 1.87 mm. in diameter containing neon at pressure 1 mm. (Curve A) and 11 mm. (Curve B), at ordinary temperature. In the first case no striations were visible until a temperature of over 50°C . was reached, these disappeared again at 140°C . In the second case they were visible at ordinary temperature but became invisible at 110°C . Viewed with the spectroscope in both cases the neon lines had practically disappeared above 100°C . leaving a clean mercury spectrum. It appears very strange that, with a smaller pressure of neon, striations are visible at higher temperatures.

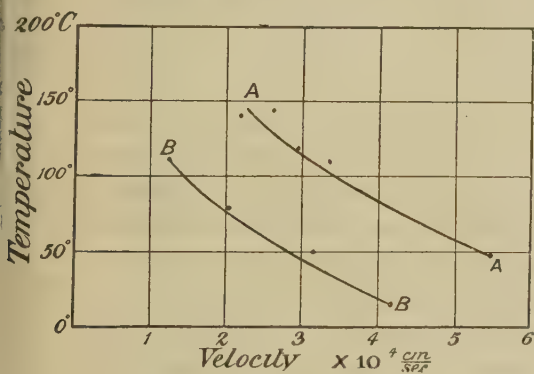


FIG. 6.

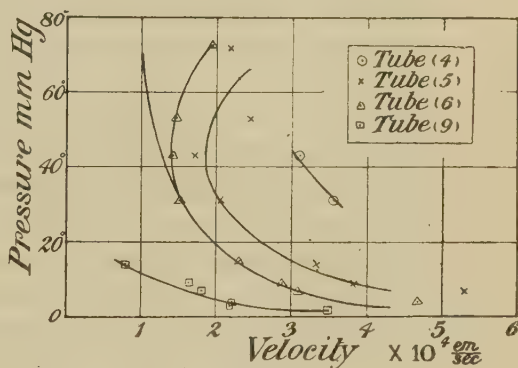


FIG. 7.

Experiments with Helium.

Helium gave much the same sort of results as neon; its striations, however, are not so easy to observe and are usually much closer together. Under certain conditions the slope was much more uniform and easier to measure than in neon. At high pressures superposed on the fine pattern of striations moving from anode to cathode there could sometimes be seen dark bands sloping the opposite ways which might be mistaken for striations moving in the reverse direction. These appear to be due to a certain condition causing weaker or slower striations, which condition progresses along the tube from cathode to anode.

The relation between velocity and pressure is represented in fig. 8. Tube 4 showed striations only at pressure between 30 mm. and 40 mm. Tubes 5, 6 and 9 exhibited them at pressures above 7, 4, and 1.5 mm. respectively. In the lower half of the curves the law of the inverse square-root

holds approximately, but at a certain pressure the velocity reaches a minimum and then increases again as the pressure is raised further. There was a slight indication of this phenomenon in the case of neon.

The following are the rough values of the velocity of the striations in helium:—

Tube 0.568 mm. in diameter		$20.1 \times p^{-1} \times 10^4$ cm./sec.
Tube 1.41 mm. in diameter		$11.6 \times p^{-1} \times 10^4$ "
Tube 1.87 mm. in diameter		$8.46 \times p^{-1} \times 10^4$ "
Tube 6.0 mm. in diameter		$4.42 \times p^{-1} \times 10^4$ "

Experiments with Mercury Vapour.

As the explanation proposed below suggests that moving striations would be conspicuous in monatomic gases with definite ionising potentials, experiments were tried with mercury vapour in a tube 1.87 mm. wide, but no trace of them could be detected.

Experiments with other Gases.

Neither air nor hydrogen showed moving striations in capillary tubes, but in a tube 1.6 mm. wide both developed stationary ones at 1 mm. to 2 mm. pressure. As the pressure was reduced these became indistinct, especially at the anode end, and using the rotating mirror moving striations could be seen. These latter became more distinct, faster and further apart, until at low pressure the discharge became an instantaneous flash.

The experimental results are so far insufficient to enable any satisfactory theory to be put forward, but further experiments are now in progress in which the current density is controlled and the potential measured, from which it is hoped to obtain more definite information.

In conclusion, the authors wish to express their best thanks to Prof. Sir Ernest Rutherford for his kind interest and advice during this research.

A Re-examination of the Light scattered by Gases in respect of Polarisation. II.—*Experiments on Helium and Argon.**

By LORD RAYLEIGH, F.R.S., Professor of Physics, Imperial College of Science, South Kensington.

(Received July 9, 1920.)

§ 1. *Helium: Method of Keeping Gas Pure.*

This gas, owing to its small refractivity, scatters so little light that purity becomes of the first importance. As is well known, the best method of purification is by cooled charcoal, according to the method of Dewar.

To use it to the best advantage, a convective circulation was maintained which delivered a stream of freshly purified gas into the region where the primary beam traversed it. A charcoal vessel was used about 2 inches diameter and 8 inches long, containing 100 gm. of coarsely granulated charcoal, a perforated zinc fitting, as shown, prevented the charcoal from dropping out at the bottom. The connections were as shown in the figure and fitted on to the brass cones of the vessel, fig. 6 of previous paper.† The liquid air was contained in a special vacuum vessel, which had an exit at the bottom as shown. The vessel was made of silica, as a glass vessel of this shape could hardly be expected to stand the strains which would result from cooling. The rubber cork at Z was in two halves to make assemblage easier, and a layer of vaseline, melted and poured on the top of it, held the liquid air satisfactorily.‡ The weight of the vacuum vessel with the liquid air contained, was taken on the rubber cork, which kept it well pressed home. As to the remaining supports of the vacuum vessel and the rubber cork, it will suffice to mention that they were carefully arranged to avoid unnecessary constraints.

The cold and heavy gas pouring down off the charcoal passed through a filter, T, of fine wire gauze about 2 inches square, before entering the space where it was traversed by the primary beam. This was designed to break up and diffuse the stream, and prevent it being localised in a thin trickle.

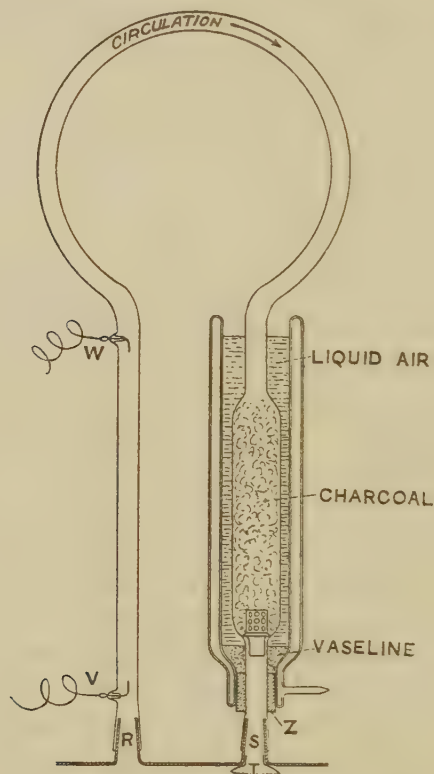
The glass work ended in ground female cones fitted to the brass male cones on the scattering vessel, to which they were cemented. The glass tube was bent as shown to give elasticity. Its internal diameter was $\frac{5}{8}$ inch. Two

* Paper I of which this is a continuation is published in 'Roy. Soc. Proc., A, vol. 97, p. 435 (1920).

† 'Roy. Soc. Proc., A, vol. 97, p. 145 (1920).

‡ I owe this expedient to Sir James Dewar.

platinum wires, 9 inches apart, were sealed in at W, V, as shown. These were to test the purity of the helium by the peculiar character of the electric



discharge through this gas at atmospheric pressure. The helium introduced in the first instance was as pure as was easily attainable, but the alternative spark in air was about 2 inches long, and the discharge showed a streaky form, with a rosy colour, probably due to nitrogen contamination. After the charcoal had been in action for about an hour, the alternative spark had fallen to $\frac{1}{2}$ inch—the least value ever attained, however long the treatment continued. At the same time the appearance had changed and had become very characteristic. On the tip of each electrode there was a golden glow due to the D_3 line, and between the electrodes there stretched a band of very faintly luminous discharge which swelled out to fill the entire diameter of the tube with a diffuse luminosity. No trace of thread-like concentration along the axis remained.

§ 2. *Comparison of Total Intensity with Helium and Air.*

In the earlier paper* comparisons were given of the total intensity of the scattered light (that is to say without distinction as to the direction of polarisation) from various gases. The expected relation with the refractivity (intensity $\propto (\mu - 1)^2$) was confirmed. The case of helium was not dealt with, however, and it appeared very desirable to examine this case, on account of the small refractivity of helium, even when compared with hydrogen.

The method adopted formerly was to use a mercury lamp as a constant source of light and to diaphragm the lens so as to equalise the intensities of scattered light when the apparatus was filled, first with, *e.g.*, hydrogen, then with air. In the case of helium it was impracticable to work with the mercury lamp, which is not bright enough for the purpose: for the scattered light from helium may be expected to be only about one-seventieth of that from air. It was necessary to fall back on the ordinary carbon arc as used for the polarisation experiments. Unfortunately this source of light is subject to great and uncontrollable variations of brightness. In preliminary tests with a photo-electric cell, it was found that the random and often sudden variations amounted to at least ± 50 per cent. of the mean value, using the hand lamp, and working with given carbons. As the carbons burn down and new ones have to be used, even greater variations may perhaps be introduced.† An automatic lamp was tried, but was certainly no steadier than the hand lamp.

Under these circumstances no great accuracy in the comparisons could be expected. It was hoped, however, that the variations would average out to a considerable extent during an hour's exposure, and that the results obtained might not be altogether without value.

The helium was kept purified throughout the experiments by cooled charcoal, with convective circulation as before. Since it would have been very inconvenient to change over often from air to helium, a number of plates were exposed for one hour (with lens at full aperture) while the apparatus was filled with helium, and were put away undeveloped. Air was then substituted, and then one hour exposures made with various small diaphragms in the lens, on each plate. After development, the densities were measured on the photo-electric apparatus, and by interpolation the aperture was found, which would have given with air, the same intensity which the full aperture gave with helium.

* 'Roy. Soc. Proc.,' A, vol. 95, p. 155 (1918).

† These variations are unimportant in the polarisation experiments, as they affect both images equally.

The following table gives the results:—

Plate No.	Helium, 31·2 mm. aperture.	Air.			Intensity, Helium/Air.
		5·1 mm. aperture.	4·07 mm. aperture.	3·18 mm. aperture.	
1	74	65	70·25	81	0·0146
2	125·5	88·5	114	143	0·0144
3	75·8	66·5	81	97	0·0203
4	72·5	59	75·25	87	0·0186

The mean value for the intensity ratio helium/air is 0·0170. The theoretical value obtained by comparison of the square of the refractivities is 0·0144. Although only one of the plates gives a value as low as this, the experimental evidence for any real discrepancy is not enough to go upon: especially if we take into account that the helium, being colder, and therefore denser, will tend to give too high a value. This point was overlooked in designing the experiment. I regard the determinations as approximately confirming the theoretical relation, which, it will be remembered, is itself only approximate, depending as it does on the assumption of spherical symmetry in the scattering particles.

§ 3. *Comparison of Polarisation in Helium.*

The result obtained before* for the comparative intensity of the two polarisations in helium was 0·42, a much higher result than for any other gas, and approximating to the value 0·5 which would be appropriate to molecules which behaved as linear oscillators. This result was wholly erroneous.† I think that the error arose from the previous use of organic vapours in the apparatus. Although this danger was appreciated at the time‡ and every attempt was made to remove such vapours by prolonged washing out with a current of air, it seems probable that some traces lingered and gave rise, under the influence of light, to a very sparse but relatively coarse fog, which would scatter very imperfectly polarised light. It must not be forgotten that the total scattered light from helium is excessively small, and that a fog which would be inappreciable in other cases would here be of importance.

The great advantage of maintaining a current of gas is that any incipient fog is continually swept away. This is practically achieved by the method of convective circulation now used.

* 'Roy. Soc. Proc.,' A, vol. 95, p. 155 (1918).

† The correction was made first in 'Nature,' December 29, 1919.

‡ *Loc. cit.*, p. 163.

Helium was first tested qualitatively, making use of the double image prism only (nicol away): $4\frac{1}{2}$ hours exposure was given. It was found that the scattered light was, to a first approximation, completely polarised. A strong image was obtained from the vibrations perpendicular to the incident beam, while nothing was perceptible from the others.

The nicol, set at 277° , was then put in, and another exposure of 26 hours was taken. The same image had still conspicuous intensity, the other being, of course, invisible as without the nicol. A further exposure of 26 hours was given with the nicol at 271° . The result was still the same, but the stronger image (perpendicular vibrations) was now only just strong enough to be detected, either visually or with the photo-electric apparatus.

The result is then that equilibrium would correspond to a setting of the nicol less than 271° (with the arbitrary zero used) or, according to the calibration experiments previously described, the weak image has certainly less than 6.5 per cent. of the intensity of the strong one.

It would be possible, by prolonging the exposure still more, to reduce this limit somewhat, but since no definite weak image has been obtained at all, the goal of obtaining a definite measurement rather than a superior limit is not in sight. The difficulty is, of course, due to the extreme faintness of the total scattering from helium, which makes the weak component (if there is one) too faint for detection.

It would be of great interest if it could be established that the weak component of helium was altogether absent, or rather, since no experiment could fully prove this, if its intensity could be shown to be less than, say, $1/1000$ th of the intensity of the strong component. But, even if the fact be so, I do not think the experimental proof would be feasible at present. Even the present much more limited conclusion has not been reached without effort.

§ 4. *Argon.*

The old experiments with this gas gave about the same value as air, but my subsequent experiments have led to quite a different result. I think that, as with helium, in this case also a fog must have been developed by some impurity in the gas.*

The argon used was obtained from the Osram lamp works, where it is used for

* There is some confirmation for this view. The argon formerly used, which was, I believe, of French origin, had been put away in bottles over water. In the course of the present experiments these bottles were emptied in order to store the new argon, which was known to be freer from nitrogen, and therefore better worth keeping. A very definite smell of hydrogen sulphide was noticed in emptying the old bottles. The presence of a trace of this gas would quite account for a fog giving misleading results.

filling incandescent lamps. The purity was the best that their plant (which depends on rectification of liquid air) could give, the nitrogen-content being stated as 2.5 per cent. The optical determination was made first with the gas as received, and the reading of the nicol for equalising the two polarisations was taken approximately, and was found to be 263.5° . This is considerably lower than had been encountered with any of the common gases, and did not agree with the result of 1918. To see whether any condensable impurity was present, the gas was passed over cooled charcoal. An appreciably lower reading still was now obtained, pointing to the removal of some impurity having an appreciable effect. Further investigation showed that this was carbon dioxide, which was present to the extent of 1 per cent.

The gas was accordingly bubbled slowly through three spiral tubes containing saturated caustic alkali, then dried and passed into the previously exhausted observation vessel.

The measurement of density of several photographs showed that the position of balance was 262.75° , the apparatus being in all respects as in the previous work on the common gases. The lowest angle found in that work was hydrogen 268.47° . It appears, therefore, that argon polarises much more perfectly than any of the common gases.

To deduce the ratio of polarisation corresponding to this setting, the method of calibration described in the previous paper* was not applicable. The difficulty arises from false light, which with so near an approach to complete polarisation, involves a correction comparable with the whole quantity to be measured. It appears best, therefore, to fall back on the assumption that the polarising prisms behave ideally, that is, that the double image prism introduces no bias, and that the nicol resolves the vibrations according to the cosine law, without any complication due to reflexion or absorption. It is certain that the double image prism does introduce bias, as the two images from an unpolarised source are measurably unequal in intensity, but the error thus introduced is probably not very important in the present case, when, owing to the extreme faintness of what may be called the abnormal component intensity, less accuracy can be looked for than in the common gases.

The position of extinction from an unpolarised source was determined usually as 258.4° , thus the angle measured from this, as a zero, which equalises the two images for argon, is $262.75^\circ - 258.4^\circ = 4.35^\circ$. Thus the ratio of intensities is $\tan^2 4.35^\circ = 0.00578$. The weak image is a little over 1 per cent. of the intensity of the strong one.

* 'Roy. Soc. Proc.,' A, vol. 97, p. 448 (1920).

It is necessary to correct this figure for the nitrogen present. It would, of course, have been better theoretically to remove the nitrogen, but this would have made the work much more troublesome, and with doubtful advantage, in practice. The estimate of the makers was 2.5 per cent. nitrogen. A rather rough determination, which I made by sparking with oxygen, and measuring the loss of volume when the oxygen had been removed, gave 3.7 per cent.

For the calculation, 3 per cent. is assumed. Further, nitrogen is assumed to scatter more light than an equal volume of argon in the ratio 1.10, the two polarisations for nitrogen being in the ratio 0.0406. On this basis, the corrected ratio of the two polarisations for argon becomes 0.0046, less than half of 1 per cent.

This figure is much lower than that found for any of the other gases, and shows that the monatomic argon molecule approximates more closely to behaving like a dielectric sphere. Although the residual polarisation is very small, and its value seriously dependent on the amount of nitrogen impurity, which is not easy to measure, yet I do not think it can be explained away.

It is hoped that the results here given will be of value in the future for testing theories of molecular and atomic structure, when these are sufficiently developed for the test to be applied. The lack of complete polarisation indicates that the molecules are not of spherical symmetry, but that they have certain preferential deviations of vibration. In general, there will be three principal axes to the particle, with corresponding coefficients of radiation, but the experimental data do not afford material for comparing these coefficients in the general case. If we assume the molecule to be symmetrical about an axis, there are then only two coefficients to be compared, and the ratio of these can be calculated from the ratio of intensities of the two polarisations, subject to an ambiguity dependent upon whether the coefficient radiation along the axis of symmetry is taken as a maximum or a minimum—whether we take the molecule as prolate or oblate. The calculation in this case, as well as in the more general one, was given by my father.* It is probable, however, that the present data will be more advantageously used in the converse way, starting with some hypothesis as to the constitution of the atom and molecule which would allow a value of the polarisation to be calculated for comparison with the experimental result.

* 'Phil. Mag.', vol. 35, p. 373 (1918).

For convenience, the results of this paper and its predecessor are here recapitulated.

Gas.	Weak component polarisation (strong component = 100).
Argon	0·46
Hydrogen	3·83
Nitrogen	4·06
Air.....	5·0
Oxygen	9·4
Carbon dioxide.....	11·7
Nitrous oxide	15·4
Helium	Not definitely determined, but < 6·5

The total intensities of light scattered by helium and by air have been compared. The ratio found was 0·0170. Considering the difficulty of the experiment, this is considered to agree within the limit of error with the ratio of the squares of refractivities, which is 0·0144.

Reduction of Error by Linear Compounding.

By W. F. SHEPPARD, Sc.D., LL.M.

(Communicated by Prof. E. T. Whittaker, F.R.S.—Received April 23, 1920.)

(Abstract.)

If $u_1, u_2, u_3, \dots$ are observed values of a single quantity U —if, in other words, there are observed values of U containing errors $u_1-U, u_2-U, u_3-U, \dots$ —, we may take as an approximate value of U any function of the u 's which, if each of the u 's in it were replaced by U , would itself become identically U . Usually this function is a linear compound (linear function) of the u 's, and is called a weighted mean: and we regard as the best weighted mean that in which the constants of the function are chosen so that it shall have the least possible mean square of error. The principle applies also when the u 's, instead of being observations of a single quantity U , are observations of a set of quantities $U_1, U_2, U_3, \dots$; with the modification that the effect of replacing (say) u_1 by a function of the u 's will be that, if the u 's in the function were put equal to the corresponding U 's, the function would not become identically equal to U_1 , but only approximately equal to

it. In the particular case in which the differences of the u 's successively diminish, a permissible form of the function is the sum of u_1 and a linear compound of the differences of the u 's of sufficiently high order.

The problem considered in this paper is the slightly more general one of improving a quantity by adding to it a linear compound of certain other quantities, called auxiliaries; the improved value being taken to be the value of this sum when, by suitable choice of the coefficients of the auxiliaries, its m.s.e. (mean square of error) is a minimum. Allied to this, and leading to a similar solution, is the problem of fitting to a set of observations $u_1, u_2, u_3, \dots$, by the method of least squares, a linear compound of a smaller number of functions of 1, 2, 3, ..., with coefficients to be determined.

The most simple case is that in which the errors of the u 's are independent—or at any rate the m.p.e. (mean product of errors) of every pair of different u 's is 0—and the m.s.s.e. are all equal to 1. The errors are then said to form a standard system. In two papers published a few years ago, on "Reduction of Errors by Means of Negligible Differences" and "Fitting of Polynomial by Method of Least Squares," I investigated the problem for this class of cases, the auxiliaries being taken to be the differences of the u 's beyond those of a certain order. The scope of the present paper is wider, and the methods also are simpler. The simplification is effected in two ways: by brief statement of general theorems, and by a theory of conjugate sets of observations.

The fundamental theorem for reduction of error is that the m.p.e. of the improved value and each of the auxiliaries is zero. This leads not only to other general theorems, but also to simplification in dealing with particular problems. Suppose, for instance, that we require the m.s.e. of an improved value, the m.s.s.e. and m.p.p.e. of the original value and the auxiliaries being known. If we construct the m.s.e. in the usual manner, the terms will form a double series, and will involve all these m.s.s.e. and m.p.p.e. But the above theorem shows that the m.s.e. of the improved value is equal to the m.p.e. of the improved value and the original value, so that we have only to deal with a single series, involving the m.s.e. of the original value and its m.p.e. with each of the auxiliaries.

In the case of the standard system, mentioned above, the m.s.e. of each u is 1, and the m.p.e. of each pair of u 's is 0. For other cases, we construct a somewhat analogous system by taking another set of quantities $y_1, y_2, y_3, \dots$, equal in number to the u 's and connected with them by linear relations, and such that if we place the two sets in linear correspondence, thus:—

$$\begin{aligned} u_1, u_2, u_3, \dots, \\ y_1, y_2, y_3, \dots, \end{aligned}$$

the m.p.e. of corresponding quantities of the two sets will be 1 and the m.p.e. of quantities which do not correspond will be 0. Sets so related are called conjugate sets. In the case of a standard system the y 's are identical with the u 's, so that the latter may be called a self-conjugate set.

If there is a second set of quantities $\delta_1, \delta_2, \delta_3, \dots$, also connected with the u 's by linear relations, there are converse linear relations between the conjugates of the δ 's and of the u 's. In particular, if the δ 's are successive differences of the u 's, and if the conjugates of the δ 's are $\sigma_1, \sigma_2, \sigma_3, \dots$, the σ 's are sums, of successive orders, of the y 's. The improved values of any specified δ 's, using the remaining δ 's as auxiliaries, are linear compounds of the σ 's which correspond to the former. Hence, if the u 's are a self-conjugate set, and the δ 's are their differences, the improved values of any linear compounds of the u 's, using certain δ 's as auxiliaries, are linear compounds of the σ 's which correspond to the other δ 's. Since the moments of the u 's, like the σ 's, are linear compounds of successive sums of the u 's, this means that the improved values are linear compounds of the moments; and it explains the appearance of the moments in this connection.

The earlier part of the paper deals with the main theorems relating to conjugate sets and to reduction of error, and with the relation of reduction of error to fitting. Certain general formulæ are then established, by means of which the solution of the problem for any particular type of data can be completed if the values of certain quantities can be found. The paper concludes with the application of the general formulæ to the particular case of the self-conjugate set. Some of the formulæ thus obtained are, of course, equivalent to formulæ obtained in the two earlier papers; but the methods of these are to a large extent superseded by the more general and more compact methods of the present paper.

Monoclinic Double Selenates of the Copper Group.

By A. E. H. TUTTON, D.Sc., M.A., F.R.S.

(Received June 2, 1920.)

This memoir deals with the four double selenates of the series $R_2M(SeO_4)_2 \cdot 6H_2O$, in which M is copper and R is potassium, rubidium, caesium, and ammonium. Only the potassium and ammonium salts of this copper group have been hitherto investigated. Their crystals were measured by Haldor Topsøe,* and their optical properties were partially investigated by Topsøe and Christiansen.†

The selenic acid employed was prepared specially for this investigation by Messrs. Hopkin and Williams, and the author's thanks are due to Mr. Edmund White for undertaking and successfully completing the preparation, which has proved to be of remarkable purity and eminently suitable for this research.

The copper selenate required was prepared by precipitating a known quantity of copper hydrate from a solution of pure copper sulphate, by means of only a very slight excess of pure sodium hydrate solution, and dissolving it, after very complete and prolonged washing, in the calculated quantity of the selenic acid.

The potassium and ammonium selenates used were part of a large stock previously prepared for the investigation of those salts. The rubidium and caesium selenates were prepared by dissolving the pure carbonates of the two metals in selenic acid, boiling off carbon dioxide and filtering. To prepare the double salts, solutions of the calculated molecular quantities of the two constituent simple salts were mixed, in the presence of one drop of excess of selenic acid. The solutions were first concentrated to the metastable condition without heating, and they then deposited eventually in all cases the required hexahydrated crystals of the double selenates of the copper group. Some crops were affected by more or less opacity of the crystals, but a sufficient number of excellent crops were obtained comparatively free from this defect (and with numerous individual crystals entirely limpid), to which these copper salts are somewhat prone. The crystals of all four double salts possess a light blue colour.

* 'Krystallogr.-kem. Unders. o. de Selensure Salte,' Copenhagen, 1870.

† 'Ann. de Chim. et de Phys.,' Ser. 5, vol. 1, pp. 84 and 86 (1874).

Potassium Copper Selenate, $K_2Cu(SeO_4)_2 \cdot 6H_2O$.*Crystal System*.—Monoclinic. Class No. 5, holohedral-prismatic.*Axial Angle*.— $\beta = 103^\circ 25'$. Topsøe's value $103^\circ 19'$.*Ratio of Axes*.— $a : b : c = 0.7508 : 1 : 0.5143$.Topsøe's values $0.7489 : 1 : 0.5230$.

Forms observed.— $a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $p'\{120\}$, $q\{011\}$, $m\{021\}$, $s'\{\bar{1}01\}$, $r'\{\bar{2}01\}$, $o\{111\}$, $o'\{\bar{1}11\}$, $n\{121\}$, $n'\{\bar{1}21\}$. The forms b , m , s' , o , o' , n , and n' , were not observed by Topsøe.

Habit.—Short prismatic parallel to the vertical axis c , or tabular parallel to $c\{001\}$. Many crops consist of simple monoclinic six-faced blocks, formed by the two forms $c\{001\}$ and $p\{110\}$, very slightly modified by small faces of $q\{011\}$ and $r'\{\bar{2}01\}$.

Other crops, however, consist of crystals on which, besides the above four forms, minute faces of a considerable number of other forms are present. Crops consisting of somewhat large crystals are especially rich in faces. On some of these crystals the prism $p'\{120\}$ formed quite broad strips, and the primary orthopinakoid $a\{100\}$ was often likewise quite prominent, these features being clearly exhibited on the typical crystal represented in fig. 1.

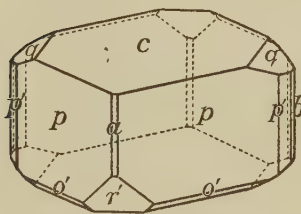


FIG. 1.

Both $n\{121\}$ and $n'\{\bar{1}21\}$, and also $o'\{\bar{1}11\}$, have been occasionally found well developed, but $b\{010\}$, $m\{021\}$, $s'\{\bar{1}01\}$, and $o\{111\}$ were all exhibited only as very small or narrow faces. On the whole, however, this salt

affords crystals which are richer in faces than has usually been the case with other members of the double selenate series, such, for instance, as the cobalt group described last year.* It is interesting that potassium copper sulphate was also observed to be exceptionally rich in faces.

* Interfacial Angles of Potassium Copper Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of Topsøe.
$ac = (100) : (001) \dots$	10	$76^\circ 30' - 76^\circ 41'$	$76^\circ 35'$	$76^\circ 35'$	0	$76^\circ 41'$
$as = (100) : (101) \dots$	—	—	—	$46^\circ 42'$	—	—
$sc = (101) : (001) \dots$	—	—	—	$29^\circ 53'$	—	—
$cr' = (001) : (201) \dots$	24	$62^\circ 41' - 63^\circ 14'$	$62^\circ 59'$	$62^\circ 55'$	4	$63^\circ 29'$
$cs' = (001) : (\bar{1}01) \dots$	—	—	—	$38^\circ 24'$	—	—
$s'r' = (\bar{1}01) : (201) \dots$	—	—	—	$24^\circ 31'$	—	—
$r'a = (201) : (100) \dots$	8	$40^\circ 15' - 40^\circ 53'$	$40^\circ 26'$	$40^\circ 30'$	4	$39^\circ 51'$
$r'c = (201) : (001) \dots$	24	$116^\circ 42' - 117^\circ 13'$	$117^\circ 1'$	$117^\circ 5'$	4	$116^\circ 31'$

* Roy. Soc. Proc., A, vol. 96, p. 156 (1919).

Interfacial Angles of Potassium Copper Selenate—*continued*.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of Topsee.
$\{ap = (100) : (110) \dots$	7	$36^{\circ} 2' - 36^{\circ} 16'$	$36^{\circ} 10'$	$36^{\circ} 7'$	3	$36^{\circ} 5'$
$pp' = (110) : (120) \dots$	15	$19^{\circ} 21' - 19^{\circ} 38'$	$19^{\circ} 30'$	$19^{\circ} 28'$	2	$19^{\circ} 28'$
$p'b = (120) : (010) \dots$	4	$34^{\circ} 22' - 34^{\circ} 25'$	$34^{\circ} 24'$	$34^{\circ} 25'$	1	
$pp''' = (110) : (130) \dots$	—	—	—	$29^{\circ} 20'$	—	
$p'''b = (130) : (010) \dots$	—	—	—	$24^{\circ} 33'$	—	
$pb = (110) : (010) \dots$	2	$53^{\circ} 49' - 53^{\circ} 58'$	$53^{\circ} 55'$	$53^{\circ} 53'$	2	
$pp = (110) : (\bar{1}\bar{1}0) \dots$	23	$72^{\circ} 1' - 72^{\circ} 27'$	$72^{\circ} 15'$	*	—	$72^{\circ} 10'$
$pp = (110) : (\bar{1}\bar{1}0) \dots$	26	$107^{\circ} 35' - 107^{\circ} 55'$	$107^{\circ} 45'$	$107^{\circ} 45'$	0	$107^{\circ} 50'$
$\{cq = (001) : (011) \dots$	39	$26^{\circ} 14' - 26^{\circ} 48'$	$26^{\circ} 35'$	*	—	$26^{\circ} 58'$
$qm = (011) : (021) \dots$	2	$18^{\circ} 23' - 18^{\circ} 28'$	$18^{\circ} 25'$	$18^{\circ} 26'$	1	
$mb = (021) : (010) \dots$	3	$44^{\circ} 54' - 44^{\circ} 59'$	$44^{\circ} 56'$	$44^{\circ} 59'$	3	
$qb = (011) : (010) \dots$	2	$63^{\circ} 22' - 63^{\circ} 23'$	$63^{\circ} 23'$	$63^{\circ} 25'$	2	
$qq = (011) : (0\bar{1}\bar{1}) \dots$	15	$126^{\circ} 39' - 127^{\circ} 6'$	$126^{\circ} 51'$	$126^{\circ} 50'$	1	
$\{ao = (100) : (111) \dots$	3	$50^{\circ} 2' - 50^{\circ} 3'$	$50^{\circ} 3'$	$50^{\circ} 2'$	1	
$oq = (111) : (011) \dots$	3	$27^{\circ} 53' - 28^{\circ} 5'$	$27^{\circ} 59'$	$28^{\circ} 0'$	1	
$aq = (100) : (011) \dots$	4	$77^{\circ} 56' - 78^{\circ} 8'$	$78^{\circ} 2'$	$78^{\circ} 2'$	0	$78^{\circ} 9'$
$qo' = (011) : (\bar{1}\bar{1}1) \dots$	—	—	—	$34^{\circ} 29'$	—	
$o'a = (\bar{1}\bar{1}1) : (\bar{1}00) \dots$	—	—	—	$67^{\circ} 29'$	—	
$\{co = (001) : (111) \dots$	1	—	$35^{\circ} 40'$	$35^{\circ} 43'$	3	
$op = (\bar{1}\bar{1}1) : (\bar{1}10) \dots$	1	—	$43^{\circ} 31'$	$43^{\circ} 29'$	2	
$cp = (001) : (\bar{1}10) \dots$	40	$79^{\circ} 3' - 79^{\circ} 20'$	$79^{\circ} 12'$	*	—	$79^{\circ} 16'$
$po' = (\bar{1}10) : (\bar{1}\bar{1}\bar{1}) \dots$	2	$56^{\circ} 5' - 56^{\circ} 5'$	$56^{\circ} 5'$	$56^{\circ} 3'$	2	
$o'c = (\bar{1}\bar{1}\bar{1}) : (00\bar{1}) \dots$	2	$44^{\circ} 43' - 44^{\circ} 43'$	$44^{\circ} 43'$	$44^{\circ} 45'$	2	
$pc = (\bar{1}10) : (00\bar{1}) \dots$	40	$100^{\circ} 39' - 100^{\circ} 56'$	$100^{\circ} 49'$	$100^{\circ} 48'$	1	$100^{\circ} 44'$
$\{bn = (010) : (\bar{1}21) \dots$	—	—	—	$53^{\circ} 11'$	—	
$no = (\bar{1}21) : (\bar{1}\bar{1}\bar{1}) \dots$	—	—	—	$16^{\circ} 18'$	—	
$bo = (010) : (\bar{1}\bar{1}\bar{1}) \dots$	—	—	—	$69^{\circ} 29'$	—	
$os = (\bar{1}\bar{1}\bar{1}) : (\bar{1}01) \dots$	—	—	—	$20^{\circ} 31'$	—	
$\{bn' = (010) : (\bar{1}21) \dots$	1	—	$46^{\circ} 54'$	$47^{\circ} 0'$	6	
$n'o' = (\bar{1}21) : (\bar{1}\bar{1}\bar{1}) \dots$	1	—	$18^{\circ} 6'$	$18^{\circ} 0'$	6	
$bo' = (010) : (\bar{1}\bar{1}\bar{1}) \dots$	1	—	$65^{\circ} 6'$	$65^{\circ} 0'$	6	
$o's' = (\bar{1}\bar{1}\bar{1}) : (\bar{1}01) \dots$	—	—	—	$25^{\circ} 0'$	—	
$o'o' = (\bar{1}\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1}) \dots$	—	—	—	$50^{\circ} 0'$	—	
$\{sq = (\bar{1}01) : (011) \dots$	—	—	—	$39^{\circ} 10'$	—	
$qn' = (011) : (\bar{1}21) \dots$	4	$35^{\circ} 3' - 35^{\circ} 14'$	$35^{\circ} 9'$	$35^{\circ} 9'$	0	
$n'p = (\bar{1}21) : (\bar{1}10) \dots$	4	$49^{\circ} 19' - 49^{\circ} 25'$	$49^{\circ} 22'$	$49^{\circ} 20'$	2	
$qp = (011) : (\bar{1}10) \dots$	35	$84^{\circ} 15' - 84^{\circ} 38'$	$84^{\circ} 28'$	$84^{\circ} 29'$	1	$84^{\circ} 12'$
$ps = (\bar{1}10) : (\bar{1}0\bar{1}) \dots$	—	—	—	$56^{\circ} 21'$	—	
$pq = (\bar{1}10) : (0\bar{1}\bar{1}) \dots$	35	$95^{\circ} 18' - 95^{\circ} 46'$	$95^{\circ} 31'$	$95^{\circ} 31'$	0	
$\{s'q = (\bar{1}01) : (011) \dots$	2	$45^{\circ} 9' - 45^{\circ} 42'$	$45^{\circ} 26'$	$45^{\circ} 30'$	4	
$qn = (011) : (\bar{1}21) \dots$	—	—	—	$27^{\circ} 16'$	—	
$np = (\bar{1}21) : (\bar{1}10) \dots$	—	—	—	$37^{\circ} 11'$	—	
$qp = (011) : (\bar{1}10) \dots$	32	$64^{\circ} 13' - 64^{\circ} 37'$	$64^{\circ} 27'$	$64^{\circ} 27'$	0	$64^{\circ} 20'$
$ps' = (\bar{1}10) : (\bar{1}0\bar{1}) \dots$	2	$69^{\circ} 50' - 70^{\circ} 21'$	$70^{\circ} 6'$	$70^{\circ} 3'$	3	
$pq = (\bar{1}10) : (0\bar{1}\bar{1}) \dots$	32	$115^{\circ} 21' - 115^{\circ} 48'$	$115^{\circ} 33'$	$115^{\circ} 33'$	0	
$\{r'o' = (201) : (\bar{1}\bar{1}\bar{1}) \dots$	2	$34^{\circ} 18' - 34^{\circ} 26'$	$34^{\circ} 22'$	$34^{\circ} 27'$	5	
$o'm = (\bar{1}\bar{1}\bar{1}) : (021) \dots$	2	$36^{\circ} 35' - 36^{\circ} 53'$	$36^{\circ} 44'$	$36^{\circ} 47'$	3	
$mp = (021) : (\bar{1}10) \dots$	2	$56^{\circ} 34' - 56^{\circ} 52'$	$56^{\circ} 43'$	$56^{\circ} 40'$	3	
$o'p = (\bar{1}\bar{1}\bar{1}) : (\bar{1}10) \dots$	3	$93^{\circ} 23' - 93^{\circ} 39'$	$93^{\circ} 31'$	$93^{\circ} 27'$	4	
$pr' = (\bar{1}10) : (20\bar{1}) \dots$	28	$51^{\circ} 51' - 52^{\circ} 20'$	$52^{\circ} 1'$	$52^{\circ} 6'$	5	$51^{\circ} 39'$
$r'p = (201) : (\bar{1}10) \dots$	26	$127^{\circ} 42' - 128^{\circ} 6'$	$127^{\circ} 58'$	$127^{\circ} 54'$	4	
Total number of measurements from 10 crystals	512					

Cleavage.—Excellent parallel to $r'\{201\}$, as usual throughout the series. A good cleavage was also discovered parallel to $b\{010\}$, the cleaved surfaces yielding excellent images of the goniometer signal exactly at $180^\circ 0'$ from the natural b -faces.

Relative Density.—Six determinations were made by the immersion method using methylene iodide and benzene mixture.

I.	Density for $17^\circ 5/4^\circ$		2.5434	For $20^\circ/4^\circ$		2.5428
II.	"	$17^\circ 5/4^\circ$		"		2.5366
III.	"	$17^\circ 4/4^\circ$		"		2.5372
IV.	"	$17^\circ 4/4^\circ$		"		2.5382
V.	"	$17^\circ 4/4^\circ$		"		2.5413
VI.	"	$16^\circ 9/4^\circ$		"		2.5355
				Mean		2.5388

Accepted value for $20^\circ/4^\circ$**2.539.**

$$\text{Molecular Volume.}—\frac{M}{d} = \frac{532.32}{2.539} = 209.66.$$

Topsøe found the specific gravity 2.527, a value much too low, and the molecular volume correspondingly much too high, 212.3.

Molecular Distance Ratios (topic axial ratios).—

$$\chi : \psi : \omega = 6.1819 : 8.2338 : 4.2347.$$

Orientation of Optical Ellipsoid.—Plane of optic axes $b\{010\}$. Sign of double refraction, negative. The first median line is the α axis of the indicatrix, and the second median line is γ .

Extinction Direction (Axis α) in Symmetry Plane.

Plate I..... $0^\circ 7'$, Plate II..... $0^\circ 11'$, Mean..... $0^\circ 9'$,

in front of the normal to $c(001)$. The direction is for this salt the first

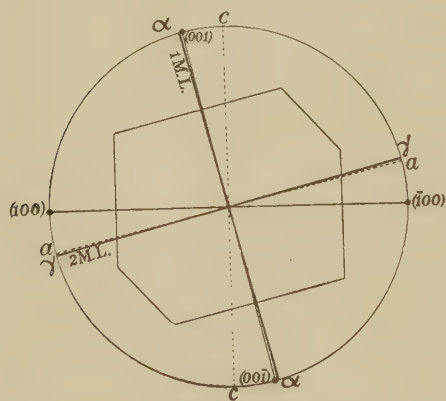


Fig. 2.

median line, which is thus $13^\circ 34'$ in front of the vertical axis c , the normal to $c(001)$ being $13^\circ 25'$ in front of that axis. The second median line lies $9'$ below the inclined axis a , and $13^\circ 34'$ below the normal to $a(100)$. Topsøe and Christiansen give $2^\circ 26'$ for the position of the first median line, but behind the normal to $c(001)$.

Fig. 2 will render the position clear. The slight angle of $9'$ between the second median line and the axis a , and between the first median line and the normal to $c(001)$ is

exaggerated in the drawing just sufficiently to show them clear of each other in each case.

Optic Axial Angle.—Determined with three pairs of plates ground perpendicular to the first and second median lines. The angle in air 2E is invisible, owing to the magnitude of the true angle.

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed 2H _a .	No. of plate perp. 2 M.L.	Observed 2H _b .	Calculated 2V _a .	Mean 2V _a .
Li.....	{ 1	79 41	1a	81 16	89 4	88 49
	{ 2	79 26	2a	82 3	88 28	
	{ 3	79 32	3a	81 19	88 56	
C	{ 1	79 36	1a	81 16	89 1	88 46
	{ 2	79 20	2a	82 3	88 24	
	{ 3	79 27	3a	81 19	88 54	
Na	{ 1	79 2	1a	81 16	88 40	88 27
	{ 2	78 48	2a	82 3	88 4	
	{ 3	78 59	3a	81 19	88 37	
Tl	{ 1	78 23	1a	81 16	88 16	88 3
	{ 2	78 10	2a	82 3	87 42	
	{ 3	78 18	3a	81 19	88 12	
Cd	{ 1	77 56	1a	81 16	88 0	87 55
	{ 2	78 1	2a	82 3	87 36	
	{ 3	78 12	3a	81 19	88 8	
F	{ 1	77 28	1a	81 16	87 42	87 36
	{ 2	77 32	2a	82 3	87 18	
	{ 3	77 40	3a	81 19	87 48	

Topsøe and Christiansen give 88° 12' as the angle 2V_a for sodium light.

Dispersion of the Median Lines.—This was determined by immersion in monochlorbenzene, the refractive index of which, 1·5248 for Na light, is nearly identical with the mean index of the crystals, 1·5226. The dispersion is very small, one determination affording 7 minutes and another with a different crystal 10 minutes of arc, for the position of the first median line, nearer to the vertical axis *c* for red C-light than for green cadmium light.

Refractive Indices.—Results with six 60°-prisms, each ground to yield two indices.

Refractive Indices of Potassium Copper Selenate.

Light.	<i>α</i> .	<i>β</i> .	<i>γ</i> .
Li	1·5063	1·5190	1·5312
C	1·5068	1·5195	1·5317
Na	1·5101	1·5228	1·5349
Tl	1·5132	1·5266	1·5386
Cd	1·5150	1·5286	1·5406
F	1·5171	1·5308	1·5428
G	1·5230	1·5368	1·5491

Mean of *α*, *β*, and *γ* for Na light = 1·5226.

α = Vibration direction parallel to first median line, 13° 34' in front of axis *c*.

β = " " " symmetry axis *b*.

γ = " " " second median line, 0° 9' below axis *α*.

Double refraction, Na_{γ-α} = 0·0248.

General formula for β , corrected to a vacuum :—

$$\beta = 1.5076 + \frac{479\ 476}{\lambda^2} + \frac{2\ 154\ 300\ 000\ 000}{\lambda^4} + \dots$$

The α indices are also approximately reproduced by the formula if the constant 1.5076 be diminished by 0.0130, and the γ indices if it be increased by 0.0121.

Observations at 70° indicated that the refractive indices diminish by about 0.0020 for a rise of 60° of temperature.

The values of Topsøe and Christiansen were: for β , line C 1.5203, line D 1.5235, line F 1.5320; the α and γ values were only obtained indirectly and for line D only; they are given as 1.5096 and 1.5385.

Axial Ratios of the Optical Ellipsoid—

$$\alpha : \beta : \gamma = 0.9917 : 1 : 1.0080, \quad a : b : c = 1.0084 : 1 : 0.9921.$$

Molecular Optical Constants.

	Axis of optical indicatrix.	α .	β .	γ .
Lorenz	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n$	{ C 0.1172	0.1196	0.1220
		{ G 0.1203	0.1230	0.1253
	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$	{ C 62.37	63.69	64.94
		{ G 64.05	65.46	66.70
	Specific dispersion, $n_D - n_C$	0.0031	0.0034	0.0033
Gladstone...	Molecular dispersion, $m_D - m_C$	1.68	1.77	1.76
	Molecular refraction, $\frac{n-1}{d} M$	C 106.26	108.92	111.48

Mean molecular refraction (Gladstone), $\frac{1}{3} (\alpha + \beta + \gamma) = 108.89$.

Rubidium Copper Selenate, $\text{Rb}_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Axial Angle.— $\beta = 104^\circ 44'$.

Ratio of Axes.— $a : b : c = 0.7495 : 1 : 0.5066$.

Forms observed.— $a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $p'\{120\}$, $p'''\{130\}$, $q\{011\}$, $r'\{201\}$, $o'\{111\}$.

Habit.—More or less tabular parallel to $c\{001\}$, but with the faces of $q\{011\}$ quite large. It is intermediate between the habits of the potassium and caesium salts. Fig. 3 represents a typical crystal.

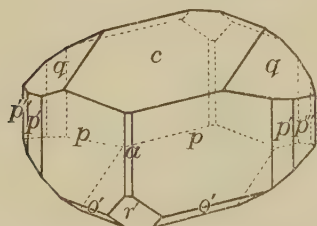


FIG. 3.

The three forms $c\{001\}$, $p\{110\}$, and $q\{011\}$ are prominent, more or less equally, and often in certain crops are present alone. Small faces of $r'\{201\}$ are usually developed on the crystals of other crops, but beyond these no other faces are perceptible at first sight. Closer

examination during the measurements on the goniometer, however,

Interfacial Angles of Rubidium Copper Selenate.

Angle.	No. of measure- ments.	Limits.	Mean observed.	Calcu- lated.	Diff.
$\left\{ \begin{array}{l} ac = (100) : (001) \\ as = (100) : (101) \\ sc = (101) : (001) \end{array} \right.$	6 — —	$75^{\circ} 17' - 75^{\circ} 31'$ — —	$75^{\circ} 24'$ — —	$75^{\circ} 16'$ 46 5 29 11	8
$\left\{ \begin{array}{l} cr' = (001) : (201) \\ cs' = (001) : (\bar{1}01) \\ s's' = (\bar{1}01) : (201) \end{array} \right.$	18 — —	63 11- 63 33 — —	63 20 — —	63 25 38 21 25 4	5
$\left\{ \begin{array}{l} r'a = (201) : (\bar{1}00) \\ r'c = (201) : (00\bar{1}) \end{array} \right.$	4 16	41 13- 41 19 116 30-116 46	41 17 116 41	41 19 116 35	2 6
$\left\{ \begin{array}{l} ap = (100) : (110) \\ pp' = (110) : (120) \\ p'p'' = (120) : (130) \end{array} \right.$	10 5 3	35 50- 35 58 19 12- 19 39 9 28- 10 19	35 56 19 25 9 52	35 56 19 28 9 54	0 3 2
$\left\{ \begin{array}{l} p'b = (120) : (010) \\ pp''' = (110) : (130) \\ p'''b = (130) : (010) \end{array} \right.$	— — 2	— — 24 32- 25 2	— — 24 47	34 36 29 22 24 42	— — 5
$\left\{ \begin{array}{l} pb = (110) : (010) \\ pp = (110) : (\bar{1}10) \\ pp = (110) : (\bar{1}10) \end{array} \right.$	2 22 22	53 46- 54 33 71 37- 72 4 107 56-108 19	54 9 71 52 108 9	54 4 * 108 8	5 — 1
$\left\{ \begin{array}{l} cq = (001) : (011) \\ qb = (011) : (010) \\ qq = (011) : (01\bar{1}) \end{array} \right.$	40 2 18	25 47- 26 26 63 44- 64 6 127 27-127 55	26 6 63 55 127 47	* 63 54 127 48	— 1 1
$\left\{ \begin{array}{l} ao = (100) : (111) \\ oq = (111) : (011) \\ aq = (100) : (011) \end{array} \right.$	— — —	— — —	— — —	49 20 27 28 76 48	— — —
$\left\{ \begin{array}{l} qo' = (011) : (\bar{1}11) \\ o'a = (\bar{1}11) : (\bar{1}00) \end{array} \right.$	— —	— —	— —	34 28 68 44	— —
$\left\{ \begin{array}{l} co = (001) : (111) \\ op = (111) : (110) \\ cp = (001) : (110) \end{array} \right.$	— — 40	— — 77 57- 78 27	— — 78 7	34 54 43 13 *	— — —
$\left\{ \begin{array}{l} po' = (110) : (\bar{1}11) \\ o'c = (\bar{1}11) : (00\bar{1}) \\ pc = (110) : (00\bar{1}) \end{array} \right.$	2 1 40	57 13- 57 17 — 101 38-102 3	57 15 44 42 101 53	57 16 44 37 101 53	1 5 0
$\left\{ \begin{array}{l} bn = (010) : (121) \\ no = (121) : (\bar{1}11) \\ bo = (010) : (\bar{1}11) \end{array} \right.$	— — —	— — —	— — —	53 52 16 5 69 57	— — —
$\left\{ \begin{array}{l} os = (\bar{1}11) : (\bar{1}01) \\ bo' = (010) : (\bar{1}11) \\ o's' = (\bar{1}11) : (\bar{1}01) \end{array} \right.$	— — —	— — —	— — —	20 3 65 6 24 54	— — —
$\left\{ \begin{array}{l} o'o' = (\bar{1}11) : (\bar{1}11) \\ sq = (101) : (011) \\ qp = (011) : (\bar{1}10) \end{array} \right.$	— 40 —	— 85 35- 86 5 —	— 85 52 —	38 22 85 48 55 50	— 4 —
$\left\{ \begin{array}{l} ps = (\bar{1}10) : (\bar{1}01) \\ pq = (\bar{1}10) : (01\bar{1}) \\ s'q = (\bar{1}01) : (011) \end{array} \right.$	40 40 —	93 53- 94 26 — —	94 9 — —	94 12 — 45 14	3 — —
$\left\{ \begin{array}{l} qn = (011) : (121) \\ np = (121) : (\bar{1}10) \\ qp = (011) : (\bar{1}10) \end{array} \right.$	— — 40	— — 63 29- 64 0	— — 63 45	26 48 36 54 63 42	— — 3
$\left\{ \begin{array}{l} ps' = (110) : (\bar{1}01) \\ pq = (110) : (01\bar{1}) \\ r'o' = (201) : (\bar{1}11) \end{array} \right.$	— 40 1	— 116 0-116 34 —	— 116 15 34 45	71 4 116 18 34 45	— 3 0
$\left\{ \begin{array}{l} o'p = (\bar{1}11) : (\bar{1}10) \\ pr' = (110) : (20\bar{1}) \\ r'p = (201) : (\bar{1}10) \end{array} \right.$	1 36 36	— 52 18- 52 56 127 9-127 37	92 33 52 38 127 22	92 42 52 33 127 27	9 5 5
Total number of measurements from 10 crystals	487				

occasionally revealed narrow line-faces of the orthopinakoid, $a\{100\}$, as shown in fig. 3, and of the clinopinakoid, $b\{010\}$, more rarely; also of the two prisms, $p'\{120\}$ and $p'''\{130\}$, which were sometimes fairly broad, as shown in fig. 3, and of the hemipyramid $o'\{\bar{1}11\}$, also shown in fig. 3, but only rarely were the signal images from any of these forms adequately bright for allocation to the cross-spider-lines.

Cleavage.—Parallel to $r'\{201\}$, perfect. A good cleavage was also found parallel to $b\{010\}$.

Relative Density.—Six determinations were made by the immersion method on freshly grown specially clear crystals.

I.	Density for $16^{\circ}0/4^{\circ}$	2.8388	For $20^{\circ}4^{\circ}$	2.8377
II.	" $16^{\circ}5/4^{\circ}$	2.8421	"	2.8411
III.	" $17^{\circ}3/4^{\circ}$	2.8356	"	2.8348
IV.	" $17^{\circ}0/4^{\circ}$	2.8417	"	2.8408
V.	" $17^{\circ}9/4^{\circ}$	2.8420	"	2.8414
VI.	" $19^{\circ}1/4^{\circ}$	2.8398	"	2.8395
				Mean
				2.8392

Accepted value for $20^{\circ}4^{\circ}$**2.839**.

Molecular Volume.— $\frac{M}{d} = \frac{624.42}{2.839} = 219.94$.

Molecular Distance (topic axial) ratios.—

$$\chi : \psi : \omega = 6.3179 : 8.4295 : 4.2704.$$

Orientation of Optical Ellipsoid.—Plane of optic axes, $b\{010\}$. Sign of double refraction, positive. The first median line is the γ axis of the indicatrix, and the second median line is α .

Extinction Direction (2M.L.) in Symmetry Plane.

Plate I... $8^{\circ}4'$, Plate II... $8^{\circ}22'$. Plate III... $8^{\circ}36'$, Mean... $8^{\circ}21'$, in front of the normal to $c(001)$. As that normal is $14^{\circ}44'$ in front of the

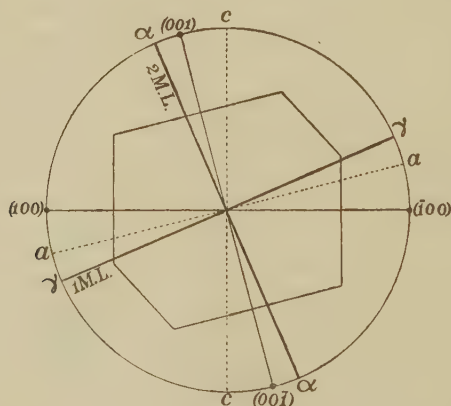


FIG. 4.

vertical axis c , the second median line lies $23^{\circ} 5'$ in front of the vertical axis c . The first median line lies $8^{\circ} 21'$ below the inclined axis a . Fig. 4 will render this clear.

Optic Axial Angle.—Results with three pairs of section-plates perpendicular to the two median lines.

Apparent Optic Axial Angle in Air, 2E, of RbCu Selenate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean 2E.
Li.....	84 45	85 2	85 33	85 7
C	84 48	85 11	85 35	85 11
Na	85 37	85 46	86 4	85 49
Tl	86 12	86 23	87 7	86 34
Cd	86 38	86 51	87 17	86 55
F	87 8	87 22	87 46	87 25

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed 2H _a .	No. of plate perp. 2 M.L.	Observed 2H _b .	Calculated 2V _a .	Mean 2V _a .
Li.....	{ 1	48 0	1a	109 54	52 50	52 57
	{ 2	48 7	2a	110 11	52 52	
	{ 3	48 20	3a	109 53	53 8	
C	{ 1	48 0	1a	109 46	52 52	52 58
	{ 2	48 7	2a	110 6	52 54	
	{ 3	48 20	3a	109 51	53 9	
Na	{ 1	48 3	1a	109 5	53 7	53 11
	{ 2	48 7	2a	109 27	53 4	
	{ 3	48 21	3a	109 13	53 21	
Tl.....	{ 1	48 4	1a	108 17	53 22	53 26
	{ 2	48 7	2a	108 32	53 20	
	{ 3	48 22	3a	108 24	53 36	
Cd	{ 1	48 5	1a	107 47	53 32	53 35
	{ 2	48 7	2a	107 58	53 30	
	{ 3	48 23	3a	107 59	53 44	
F	{ 1	48 6	1a	107 13	53 42	53 43
	{ 2	48 7	2a	107 35	53 37	
	{ 3	48 24	3a	107 38	53 51	

Dispersion of the Median Lines.—This is very small, measurements in monochlorbenzene (of similar refractive index) having indicated that the first median line lies nearer to the inclined axis a by 8 minutes for green cadmium light than for red C hydrogen light.

Effect of Temperature on Optic Axial Angle.—Determinations at a series of temperatures up to 70° C. indicated that the optic axial angle in air, 2E, increases 12° , from 86° to 98° , during this rise of temperature.

Refractive Indices.—Results obtained with six 60° -prisms, each ground to afford two indices directly.

Refractive Indices of Rubidium Copper Selenate.

Light.	α .	β .	γ .
Li.....	1·5117	1·5146	1·5280
O.....	1·5122	1·5152	1·5286
Na.....	1·5153	1·5183	1·5318
Tl.....	1·5185	1·5216	1·5354
Cd.....	1·5204	1·5237	1·5375
F.....	1·5225	1·5257	1·5396
G.....	1·5284	1·5317	1·5461

Mean of α , β , and γ for Na light = 1·5218.

α = Vibration direction parallel to second median line, 23° 5' in front of axis c .

β = " " " symmetry axis b .

γ = " " " first median line, 8° 21' below axis a .

Double refraction, $\text{Na}\gamma - \alpha = 0\cdot0165$.

General formula β , corrected to a vacuum:—

$$\beta = 1\cdot5017 + \frac{634\ 053}{\lambda^2} - \frac{1\ 524\ 900\ 000\ 000}{\lambda^4} + \dots$$

The α indices are also reproduced by the formula if the constant 1·5017 be diminished by 0·0031, and the γ indices if it be increased by 0·0135.

Observations at 70° indicated that the refractive indices diminish with rise of temperature, to the extent of 0·0020 for 60° rise of temperature in the case of γ and somewhat less for α and β .

Axial Ratios of the Optical Ellipsoid—

$$\alpha : \beta : \gamma = 0\cdot9980 : 1 : 1\cdot0089, \quad a : b : c = 1\cdot0020 : 1 : 0\cdot9912.$$

Molecular Optical Constants.

Axis of optical indicatrix.		α .	β .	γ .
Lorenz	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n \dots \dots$	C	0·1057	0·1063
		G	0·1085	0·1091
	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m \dots$	C	66·02	66·35
		G	67·77	68·12
	Specific dispersion, $n_G - n_C$		0·0028	0·0028
Gladstone ...	Molecular dispersion, $m_G - m_C$		1·75	1·77
	Molecular refraction, $\frac{n-1}{d} M$	C	112·65	113·32
				116·26

Mean molecular refraction (Gladstone), $\frac{1}{3} (\alpha + \beta + \gamma) = 114\cdot08$.

Cæsium Copper Selenate, $\text{Cs}_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Axial Angle.— $\beta = 105^\circ 42'$.

Ratio of Axes.— $a : b : c = 0\cdot7398 : 1 : 0\cdot4981$.

Forms observed.— $a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $p'\{120\}$, $q\{011\}$, $m\{021\}$, $r'\{201\}$, $o\{111\}$, $o'\{111\}$.

Habit.—Prismatic parallel to inclined axis a , the habit remarkably consistently characteristic of all the caesium salts of the series, both double selenates and double sulphates. It is due to the relatively small development, in narrow strips only, of the basal pinakoid $c\{001\}$, and relatively very large development of the primary clinodomal prism $q\{011\}$.

The end faces of the prism are formed almost entirely by the faces of the primary prism $p\{110\}$ and the orthopinakoidal form $r'\{201\}$. These two forms vary very much in relative development, so that in some crops the former are largely predominant, and the latter very small, as shown in fig. 5, while in others the r' -faces are exceptionally large and practically form the prism-end, as shown in fig. 6.

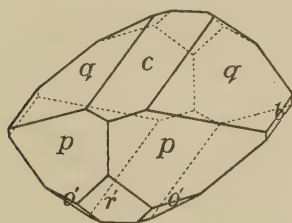


FIG. 5.

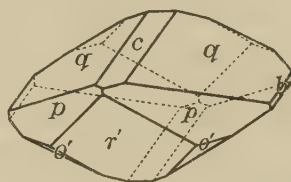


FIG. 6.

The faces of $o'\{\bar{1}11\}$ were very small, except occasionally on large crystals, and those of $o\{111\}$ were still rarer, and only once measurable. The two primary pinakoids $a\{100\}$ and $b\{010\}$ were only present as narrow lines; the forms $p'\{120\}$ and $m\{021\}$ were only observed on one of the crystals measured, as very minute faces, although clearly measurable.

Interfacial Angles of Cæsium Copper Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
$ac = (100) : (001) \dots\dots$	1	° ' — '	74° 25'	74° 18'	7
$as = (100) : (101) \dots\dots$	—	—	—	45 43	
$sc = (101) : (001) \dots\dots$	—	—	—	28 35	
$cr' = (001) : (201) \dots\dots$	20	63 10- 63 47	63 33	63 37	4
$cs' = (001) : (101) \dots\dots$	—	—	—	38 9	
$s's' = (101) : (201) \dots\dots$	—	—	—	25 28	
$r'a = (201) : (100) \dots\dots$	3	41 59- 42 22	42 9	42 5	4
$r'c = (201) : (001) \dots\dots$	20	116 17-116 53	116 27	116 23	4
$ap = (100) : (110) \dots\dots$	—	—	—	35 37	
$pp' = (110) : (120) \dots\dots$	2	19 16- 19 32	19 24	19 28	4
$p'b = (120) : (010) \dots\dots$	—	—	—	34 55	
$pp''' = (110) : (130) \dots\dots$	—	—	—	29 26	
$p''b = (130) : (010) \dots\dots$	—	—	—	24 57	
$pb = (110) : (010) \dots\dots$	4	54 21- 54 28	54 24	54 23	1
$pp = (110) : (110) \dots\dots$	20	70 52- 71 35	71 14	*	
$pp = (110) : (110) \dots\dots$	20	108 24-109 8	108 46	108 46	0

Interfacial Angles of Cæsium Copper Selenate—*continued*.

Angle.	No. of measure- ments.	Limits.	Mean observed.	Calcu- lated.	Diff.
$\left\{ \begin{array}{l} cq = (001) : (011) \\ qm = (011) : (021) \\ mb = (021) : (010) \\ qb = (011) : (010) \\ qq = (011) : (01\bar{1}) \end{array} \right.$	$\left\{ \begin{array}{l} 40 \\ — \\ — \\ 2 \\ 20 \end{array} \right.$	$\left\{ \begin{array}{l} 25^{\circ} 16' - 25^{\circ} 53' \\ — \\ — \\ 64^{\circ} 23' - 64^{\circ} 27' \\ 128^{\circ} 30' - 128^{\circ} 59' \end{array} \right.$	$\left\{ \begin{array}{l} 25^{\circ} 37' \\ — \\ — \\ 64^{\circ} 25' \\ 128^{\circ} 46' \end{array} \right.$	$\left\{ \begin{array}{l} * \\ 18^{\circ} 11' \\ 46^{\circ} 12' \\ 64^{\circ} 23' \\ 128^{\circ} 46' \end{array} \right.$	$\left\{ \begin{array}{l} ' \\ \\ \\ 2 \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} ao = (100) : (111) \\ oq = (111) : (011) \\ aq = (100) : (011) \\ qo' = (011) : (1\bar{1}1) \\ o'a = (111) : (100) \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \\ — \\ 2 \\ — \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \\ — \\ 34^{\circ} 32' - 34^{\circ} 36' \\ — \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \\ — \\ 34^{\circ} 34' \\ — \end{array} \right.$	$\left\{ \begin{array}{l} 48^{\circ} 53' \\ 27^{\circ} 0' \\ 75^{\circ} 53' \\ 34^{\circ} 27' \\ 69^{\circ} 40' \end{array} \right.$	$\left\{ \begin{array}{l} \\ \\ \\ 7 \\ \end{array} \right.$
$\left\{ \begin{array}{l} co = (001) : (111) \\ op = (111) : (110) \\ cp = (001) : (110) \\ po' = (110) : (11\bar{1}) \\ o'c = (11\bar{1}) : (00\bar{1}) \\ pc = (110) : (00\bar{1}) \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ 1 \\ 39 \\ 8 \\ 9 \\ 40 \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \\ 76^{\circ} 56' - 77^{\circ} 35' \\ 57^{\circ} 51' - 58^{\circ} 47' \\ 44^{\circ} 12' - 44^{\circ} 51' \\ 102^{\circ} 29' - 103^{\circ} 6' \end{array} \right.$	$\left\{ \begin{array}{l} 34^{\circ} 9' \\ 43^{\circ} 12' \\ 77^{\circ} 16' \\ 58^{\circ} 11' \\ 44^{\circ} 32' \\ 102^{\circ} 44' \end{array} \right.$	$\left\{ \begin{array}{l} 34^{\circ} 11' \\ 43^{\circ} 5' \\ * \\ 58^{\circ} 16' \\ 44^{\circ} 28' \\ 102^{\circ} 44' \end{array} \right.$	$\left\{ \begin{array}{l} 2 \\ 7 \\ \\ 5 \\ 4 \\ 0 \end{array} \right.$
$\left\{ \begin{array}{l} bn = (010) : (121) \\ no = (121) : (111) \\ bo = (010) : (111) \\ os = (111) : (101) \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \\ — \\ — \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \\ — \\ — \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \\ — \\ — \end{array} \right.$	$\left\{ \begin{array}{l} 54^{\circ} 30' \\ 15^{\circ} 53' \\ 70^{\circ} 23' \\ 19^{\circ} 37' \end{array} \right.$	$\left\{ \begin{array}{l} \\ \\ \\ \end{array} \right.$
$\left\{ \begin{array}{l} bo' = (010) : (1\bar{1}1) \\ o's' = (111) : (101) \\ o'o' = (111) : (1\bar{1}1) \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \\ — \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \\ — \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \\ — \end{array} \right.$	$\left\{ \begin{array}{l} 65^{\circ} 17' \\ 24^{\circ} 43' \\ 49^{\circ} 26' \end{array} \right.$	$\left\{ \begin{array}{l} \\ \\ \end{array} \right.$
$\left\{ \begin{array}{l} sq = (101) : (011) \\ qp = (011) : (110) \\ ps = (110) : (10\bar{1}) \\ pq = (110) : (01\bar{1}) \end{array} \right.$	$\left\{ \begin{array}{l} — \\ 39 \\ 39 \\ 39 \end{array} \right.$	$\left\{ \begin{array}{l} — \\ 86^{\circ} 43' - 87^{\circ} 13' \\ — \\ 92^{\circ} 38' - 93^{\circ} 22' \end{array} \right.$	$\left\{ \begin{array}{l} — \\ 86^{\circ} 59' \\ — \\ 93^{\circ} 1' \end{array} \right.$	$\left\{ \begin{array}{l} 37^{\circ} 38' \\ 86^{\circ} 57' \\ 55^{\circ} 25' \\ 93^{\circ} 3' \end{array} \right.$	$\left\{ \begin{array}{l} \\ 2 \\ \\ 2 \end{array} \right.$
$\left\{ \begin{array}{l} s'q = (101) : (011) \\ qn = (011) : (121) \\ np = (121) : (110) \\ qp = (011) : (110) \\ ps' = (110) : (10\bar{1}) \\ pq = (110) : (01\bar{1}) \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \\ — \\ 39 \\ — \\ 39 \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \\ — \\ 62^{\circ} 59' - 63^{\circ} 34' \\ — \\ 116^{\circ} 23' - 117^{\circ} 4' \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \\ — \\ 63^{\circ} 18' \\ — \\ 116^{\circ} 42' \end{array} \right.$	$\left\{ \begin{array}{l} 44^{\circ} 50' \\ 26^{\circ} 24' \\ 36^{\circ} 51' \\ 63^{\circ} 15' \\ 71^{\circ} 55' \\ 116^{\circ} 45' \end{array} \right.$	$\left\{ \begin{array}{l} \\ \\ \\ 3 \\ \\ 3 \end{array} \right.$
$\left\{ \begin{array}{l} r'o' = (201) : (1\bar{1}1) \\ o'm = (111) : (021) \\ mp = (021) : (110) \\ o'p = (111) : (110) \\ pr' = (110) : (20\bar{1}) \\ r'p = (201) : (110) \end{array} \right.$	$\left\{ \begin{array}{l} 13 \\ 1 \\ 1 \\ 12 \\ 38 \\ 38 \end{array} \right.$	$\left\{ \begin{array}{l} 34^{\circ} 36' - 35^{\circ} 29' \\ — \\ — \\ 91^{\circ} 41' - 92^{\circ} 33' \\ 52^{\circ} 30' - 53^{\circ} 14' \\ 126^{\circ} 43' - 127^{\circ} 24' \end{array} \right.$	$\left\{ \begin{array}{l} 34^{\circ} 57' \\ 36^{\circ} 27' \\ 55^{\circ} 43' \\ 92^{\circ} 11' \\ 52^{\circ} 51' \\ 127^{\circ} 9' \end{array} \right.$	$\left\{ \begin{array}{l} 34^{\circ} 54' \\ 36^{\circ} 24' \\ 55^{\circ} 49' \\ 92^{\circ} 13' \\ 52^{\circ} 53' \\ 127^{\circ} 7' \end{array} \right.$	$\left\{ \begin{array}{l} 3 \\ 3 \\ 6 \\ 2 \\ 2 \\ 2 \end{array} \right.$
Total number of measurements from 10 crystals	511				

Cleavage.—Perfect parallel $r'\{201\}$. A second good cleavage parallel to $b\{010\}$ was also discovered.

Relative Density.—Six determinations were carried out by the immersion method on crystals small and exceptionally clear.

I. Density for $16^{\circ} 2/4^{\circ}$	3.0734	For $20^{\circ} 4^{\circ}$	3.0722
II. " " $16^{\circ} 4/4^{\circ}$	3.0744	"	3.0733
III. " " $16^{\circ} 4/4^{\circ}$	3.0735	"	3.0724
IV. " " $17^{\circ} 7/4^{\circ}$	3.0708	"	3.0701
V. " " $16^{\circ} 8/4^{\circ}$	3.0770	"	3.0760
VI. " " $17^{\circ} 5/4^{\circ}$	3.0746	"	3.0738

Mean 3.0730

Accepted value for $20^\circ/4^\circ \dots 3.073$.

Molecular Volume.— $\frac{M}{d} = \frac{718.42}{3.073} = 233.79$.

Molecular Distance (topic axial) ratios.—

$$\chi : \psi : \omega = 6.4378 : 8.7022 : 4.3346.$$

Orientation of Optical Ellipsoid.—Plane of optic axes $b\{010\}$. Sign of double refraction positive. The first median line is the γ axis of the indicatrix, and the second line median is α .

Extinction Direction (2 M.L.) in Symmetry Plane.

Plate I..... $21^\circ 50'$,

Plate II..... $21^\circ 9'$,

Mean extinction angle..... $21^\circ 30'$,

in front of the normal to $c(001)$. As that normal is already $15^\circ 42'$ in front of the vertical axis c , the second median line lies $37^\circ 12'$ in front of the vertical axis c . The first median line lies $21^\circ 30'$ below the inclined axis α . Fig. 7 will render the position plain.

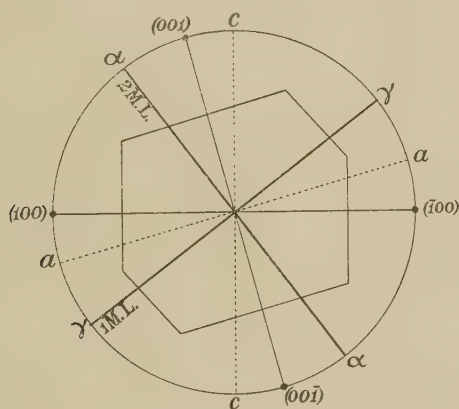


FIG. 7.

Optic Axial Angle.—Results with three pairs of plates ground perpendicular to the first and second median lines.

Apparent Optic Axial Angle in Air, 2E, of CsCu Selenate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean 2E.
Li.....°	76 44	77 28	76 49	77 0
C	76 52	77 32	76 53	77 6
Na	77 13	77 59	77 28	77 33
Tl.....°	77 39	78 15	78 3	77 59
Cd	77 49	78 41	78 23	78 18
F	78 3	79 2	78 40	78 35

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed 2H _a .	No. of plate perp. 2 M.L.	Observed 2H _c .	Calculated 2V _a .	Mean 2V _a .
Li.....	{ 1 2 3	44 7 44 33 44 13	1a 2a 3a	114 10 114 25 114 18	48 12 48 32 48 16	48 20
C	{ 1 2 3	44 6 44 32 44 12	1a 2a 3a	114 2 114 21 114 12	48 13 48 32 48 16	48 20
Na	{ 1 2 3	44 2 44 28 44 7	1a 2a 3a	113 22 113 44 113 33	48 19 48 38 48 21	48 26
Tl.....	{ 1 2 3	43 58 44 23 44 3	1a 2a 3a	112 40 112 59 112 50	48 26 48 44 48 28	48 33
Cd	{ 1 2 3	43 54 44 20 44 2	1a 2a 3a	112 13 112 31 112 22	48 29 48 49 48 34	48 37
F	{ 1 2 3	43 48 44 16 44 0	1a 2a 3a	111 35 112 3 111 49	48 33 48 52 48 41	48 42

Dispersion of the Median Lines.—This was determined by immersion of the best of the section-plates perpendicular to the first median line in oil of cloves, the refractive index of which is similar to that of the crystals. It was found that the median lines are dispersed about 8' in the symmetry plane, so that the first median line is nearer to the inclined axis *a* by 8' for red C-light than for green thallium light.

Effect of Temperature on Optic Axial Angle.—On heating one of the section-plates gradually to 75° C., the optic axial angle in air 2E proved to change only very slightly, becoming reduced by one degree only for this rise of temperature.

Refractive Indices.—Results with six 60°-prisms, each ground to afford two indices directly.

Refractive Indices of Cæsium Copper Selenate.

Light.	<i>a</i> .	<i>β</i> .	<i>γ</i> .
Li.....	1·5243	1·5259	1·5355
C	1·5248	1·5264	1·5360
Na	1·5282	1·5298	1·5394
Tl	1·5316	1·5332	1·5427
Cd	1·5335	1·5352	1·5447
F	1·5355	1·5372	1·5467
G	1·5416	1·5434	1·5530

Mean of *a*, *β*, and *γ* for Na light = 1·5325.

a = Vibration direction parallel to second median line, 37° 12' in front of axis *c*.

β = " " " symmetry axis *b*.

γ = " " " first median line, 21° 30' below axis *a*.

Double refraction, Na_{*γ-a*} = 0·0112.

General formula for the intermediate refractive index β , corrected to a vacuum (correction + 0.0004):—

$$\beta = 1.5125 + \frac{665\ 923}{\lambda^2} - \frac{1\ 784\ 800\ 000\ 000}{\lambda^4} + \dots$$

The α indices are also reproduced very closely by the formula if the constant 1.5125 be diminished by 0.0016 and the γ indices if the constant be increased by 0.0096.

Observations at 70° C. showed that the refractive indices are diminished by about 0.0017 (varying from 0.0015 to 0.0019) for 60° rise of temperature.

Axial Ratios of the Optical Ellipsoid—

$$\alpha : \beta : \gamma = 0.9990 : 1 : 1.0063, \quad a : b : c = 1.0010 : 1 : 0.9938.$$

Molecular Optical Constants.

	Axis of optical indicatrix.	α .	β .	γ .
Lorenz	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n$	C 0.0997	0.0999	0.1015
		G 0.1024	0.1026	0.1041
	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$	C 71.62	71.81	72.90
		G 73.53	73.74	74.81
	Specific dispersion, $n_D - n_C$	0.0027	0.0027	0.0026
	Molecular dispersion, $m_D - m_C$	1.91	1.93	1.91
Gladstone ...	Molecular refraction, $\frac{n-1}{d} M$	C 122.69	123.07	125.31

Mean molecular refraction (Gladstone), $\frac{1}{3} (\alpha + \beta + \gamma) = 123.69$.

Ammonium Copper Selenate $(\text{NH}_4)_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Axial Angle.— $\beta = 105^\circ 30'$. The value found by Topsøe was $105^\circ 32'$.

Ratio of Axes.— $a : b : c = 0.7476 : 1 : 0.5150$.

Topsøe's values $0.7488 : 1 : 0.5126$.

Forms observed.— $a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $p'\{120\}$, $q\{011\}$, $o\{111\}$, $o'\{\bar{1}11\}$, $r'\{\bar{2}01\}$, $n'\{\bar{1}21\}$.

The forms a , o , and n' were not observed by Topsøe.

Habit.—Usually short prismatic parallel to $p\{110\}$ and to the vertical axis c . In certain crops these prisms were considerably elongated.

As regards the relative development of $q\{011\}$ and $r'\{\bar{2}01\}$ the crystals generally much resembled those of the rubidium salt, although those of certain

crops more nearly approximated to the type of the potassium salt. One peculiarity was very common, however, namely, the elongation above referred to of the prism $p\{110\}$. A typical crystal exhibiting this feature is shown in fig. 8.

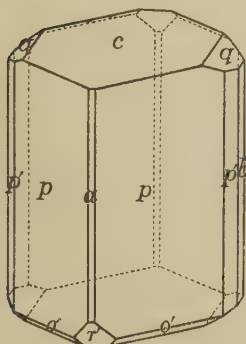


FIG. 8.

Interfacial Angles of Ammonium Copper Selenate.

Angle.	No. of measure- ments.	Limits.	Mean observed.	Calcu- lated.	Diff.	Topsøe's values.
$\left\{ \begin{array}{l} ac = (100) : (001) \dots \\ as = (100) : (101) \dots \\ sc = (101) : (001) \dots \\ cr' = (001) : (201) \dots \\ cs' = (001) : (101) \dots \\ s'q' = (101) : (201) \dots \\ r'a = (201) : (100) \dots \\ r'e = (201) : (001) \dots \end{array} \right.$	$\left\{ \begin{array}{l} 9 \\ - \\ - \\ 14 \\ - \\ - \\ 9 \\ 14 \end{array} \right.$	$\left\{ \begin{array}{l} 74 \ 25-74 \ 37 \\ - \\ - \\ 64 \ 26-64 \ 49 \\ - \\ - \\ 40 \ 41-40 \ 59 \\ 115 \ 15-115 \ 32 \end{array} \right.$	$\left\{ \begin{array}{l} 74 \ 29 \\ - \\ - \\ 64 \ 40 \\ - \\ - \\ 40 \ 50 \\ 115 \ 20 \end{array} \right.$	$\left\{ \begin{array}{l} 74 \ 30 \\ 45 \ 13 \\ 29 \ 17 \\ 64 \ 34 \\ 39 \ 9 \\ 25 \ 25 \\ 40 \ 56 \\ 115 \ 26 \end{array} \right.$	$\left\{ \begin{array}{l} 1 \\ - \\ - \\ 6 \\ - \\ - \\ 6 \\ 6 \end{array} \right.$	$\left\{ \begin{array}{l} 74 \ 28 \\ - \\ - \\ 64 \ 22 \\ - \\ - \\ - \\ 115 \ 38 \end{array} \right.$
$\left\{ \begin{array}{l} ap = (100) : (110) \dots \\ pp' = (110) : (120) \dots \\ p'b = (120) : (010) \dots \\ pp'' = (110) : (130) \dots \\ p'''b = (130) : (010) \dots \\ pb = (110) : (010) \dots \\ pp = (110) : (110) \dots \\ pp = (110) : (110) \dots \end{array} \right.$	$\left\{ \begin{array}{l} 14 \\ 8 \\ 7 \\ - \\ - \\ 23 \\ 20 \\ 20 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 32-35 \ 58 \\ 19 \ 13-19 \ 38 \\ 34 \ 37-34 \ 59 \\ - \\ - \\ 54 \ 0-54 \ 25 \\ 71 \ 20-71 \ 46 \\ 108 \ 14-108 \ 40 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 46 \\ 19 \ 24 \\ 34 \ 47 \\ - \\ - \\ 54 \ 14 \\ 71 \ 32 \\ 108 \ 28 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 46 \\ 19 \ 28 \\ 34 \ 46 \\ 29 \ 24 \\ 24 \ 50 \\ 54 \ 14 \\ * \\ 108 \ 28 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 4 \\ 1 \\ - \\ - \\ 0 \\ - \\ 0 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \\ - \\ - \\ 71 \ 37 \\ 108 \ 23 \end{array} \right.$
$\left\{ \begin{array}{l} cq = (001) : (011) \dots \\ qb = (011) : (010) \dots \\ qq = (011) : (011) \dots \end{array} \right.$	$\left\{ \begin{array}{l} 25 \\ 16 \\ 12 \end{array} \right.$	$\left\{ \begin{array}{l} 26 \ 10-26 \ 40 \\ 63 \ 24-63 \ 48 \\ 127 \ 8-127 \ 24 \end{array} \right.$	$\left\{ \begin{array}{l} 26 \ 24 \\ 63 \ 37 \\ 127 \ 15 \end{array} \right.$	$\left\{ \begin{array}{l} * \\ 63 \ 36 \\ 127 \ 12 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ 1 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ 26 \ 17 \\ - \end{array} \right.$
$\left\{ \begin{array}{l} ao = (100) : (111) \dots \\ oq = (111) : (011) \dots \\ aq = (100) : (011) \dots \\ qo' = (011) : (111) \dots \\ o'a = (111) : (100) \dots \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} 48 \ 35 \\ 27 \ 34 \\ 76 \ 9 \\ 35 \ 7 \\ 68 \ 44 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \\ - \end{array} \right.$
$\left\{ \begin{array}{l} co = (001) : (111) \dots \\ op = (111) : (110) \dots \\ ep = (001) : (110) \dots \\ po' = (110) : (111) \dots \\ o'e = (111) : (001) \dots \\ pc = (110) : (001) \dots \end{array} \right.$	$\left\{ \begin{array}{l} 3 \\ 3 \\ 40 \\ 5 \\ 5 \\ 40 \end{array} \right.$	$\left\{ \begin{array}{l} 34 \ 44-35 \ 4 \\ 42 \ 25-42 \ 45 \\ 77 \ 20-77 \ 37 \\ 56 \ 20-57 \ 32 \\ 44 \ 58-46 \ 5 \\ 102 \ 23-102 \ 39 \end{array} \right.$	$\left\{ \begin{array}{l} 34 \ 55 \\ 42 \ 35 \\ 77 \ 29 \\ 57 \ 2 \\ 45 \ 27 \\ 102 \ 31 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 0 \\ 42 \ 29 \\ * \\ 57 \ 4 \\ 45 \ 27 \\ 102 \ 31 \end{array} \right.$	$\left\{ \begin{array}{l} 5 \\ 6 \\ - \\ 2 \\ 0 \\ 0 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ 77 \ 27 \\ - \\ 45 \ 15 \\ 102 \ 32 \end{array} \right.$
$\left\{ \begin{array}{l} bn = (010) : (121) \dots \\ no = (121) : (111) \dots \\ bo = (010) : (111) \dots \\ os = (111) : (101) \dots \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} 53 \ 49 \\ 16 \ 6 \\ 69 \ 55 \\ 20 \ 5 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \end{array} \right.$
$\left\{ \begin{array}{l} bn' = (010) : (121) \dots \\ n'o' = (121) : (111) \dots \\ bo' = (010) : (111) \dots \\ o's' = (111) : (101) \dots \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} 46 \ 40 \\ 18 \ 5 \\ 64 \ 45 \\ 25 \ 15 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ - \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ 25 \ 12 \end{array} \right.$
$\left\{ \begin{array}{l} sq = (101) : (011) \dots \\ qn' = (011) : (121) \dots \\ n'p = (121) : (110) \dots \\ qp = (011) : (110) \dots \\ ps = (110) : (101) \dots \\ pq = (110) : (011) \dots \end{array} \right.$	$\left\{ \begin{array}{l} - \\ 2 \\ 2 \\ 26 \\ - \\ 26 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ 35 \ 56-36 \ 0 \\ 50 \ 15-50 \ 17 \\ 86 \ 3-86 \ 22 \\ - \\ 93 \ 36-93 \ 53 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ 35 \ 58 \\ 50 \ 16 \\ 86 \ 12 \\ - \\ 93 \ 48 \end{array} \right.$	$\left\{ \begin{array}{l} 38 \ 38 \\ 35 \ 52 \\ 50 \ 22 \\ 86 \ 14 \\ 55 \ 8 \\ 93 \ 46 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ 6 \\ 6 \\ 2 \\ - \\ 2 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ 86 \ 19 \\ - \\ - \end{array} \right.$
$\left\{ \begin{array}{l} s'q = (101) : (011) \dots \\ qn = (011) : (121) \dots \\ np = (121) : (110) \dots \\ qp = (011) : (110) \dots \\ ps' = (110) : (101) \dots \\ pq = (110) : (011) \dots \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ 25 \\ - \\ 25 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ 62 \ 47-63 \ 8 \\ - \\ 116 \ 49-117 \ 13 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ 62 \ 59 \\ - \\ 117 \ 1 \end{array} \right.$	$\left\{ \begin{array}{l} 46 \ 0 \\ 26 \ 45 \\ 36 \ 15 \\ 63 \ 0 \\ 71 \ 0 \\ 117 \ 0 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ 1 \\ - \\ 1 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ - \\ 63 \ 0 \\ - \\ - \end{array} \right.$
$\left\{ \begin{array}{l} r'o' = (201) : (111) \dots \\ o'p = (111) : (110) \dots \\ pr' = (110) : (201) \dots \\ r'p = (201) : (110) \dots \end{array} \right.$	$\left\{ \begin{array}{l} 10 \\ 10 \\ 38 \\ 38 \end{array} \right.$	$\left\{ \begin{array}{l} 34 \ 52-35 \ 22 \\ 92 \ 2-92 \ 57 \\ 51 \ 58-52 \ 26 \\ 127 \ 33-128 \ 7 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 7 \\ 92 \ 37 \\ 52 \ 8 \\ 127 \ 52 \end{array} \right.$	$\left\{ \begin{array}{l} 35 \ 14 \\ 92 \ 34 \\ 52 \ 12 \\ 127 \ 48 \end{array} \right.$	$\left\{ \begin{array}{l} 7 \\ 3 \\ 4 \\ 4 \end{array} \right.$	$\left\{ \begin{array}{l} - \\ - \\ 52 \ 23 \\ 127 \ 37 \end{array} \right.$
Total number of measurements from 10 crystals.....	489					

The faces of $a\{100\}$ and $b\{010\}$ were almost always mere lines, but occasionally the b -faces were broader strips, as in several of the small crystals measured. The faces of the forms $o\{111\}$, $o'\{\bar{1}11\}$, and $n'\{\bar{1}21\}$ were only very minute on all the crystals measured.

Cleavage.—Perfect parallel $r'\{\bar{2}01\}$. An even more excellent one was found parallel $b\{010\}$.

Relative Density.—Six determinations were made by the immersion method, with crystals freshly grown and perfectly clear.

I. Density for $16^{\circ} 7/4^{\circ}$	2.2238	For $20^{\circ}/4^{\circ}$	2.2231
II. " $16^{\circ} 5/4^{\circ}$	2.2256	" 	2.2248
III. " $16^{\circ} 2/4^{\circ}$	2.2217	" 	2.2209
IV. " $16^{\circ} 6/4^{\circ}$	2.2252	" 	2.2244
V. " $16^{\circ} 6/4^{\circ}$	2.2248	" 	2.2240
VI. " $16^{\circ} 9/4^{\circ}$	2.2227	" 	2.2220
		Mean	2.2232

Accepted value for $20^{\circ}/4^{\circ}$**2.223**.

$$\text{Molecular Volume.}—\frac{M}{d} = \frac{490.48}{2.223} = 220.64.$$

Topsøe obtained the lower value 2.221 for the specific gravity, and consequently also a molecular volume too high, namely, 222.5.

Molecular Distance (topic axial) ratios.—

$$\chi : \psi : \omega = 6.2868 : 8.4093 : 4.3308.$$

Orientation of Optical Ellipsoid.—Plane of optic axes $b\{010\}$. Sign of double refraction, negative. The first median line is the α axis of the indicatrix, and γ is the second median line.

Extinction Direction (1M.L.) in Symmetry Plane.

Plate I..... $2^{\circ} 26'$, Plate II..... $3^{\circ} 30'$, Mean..... $2^{\circ} 58'$,

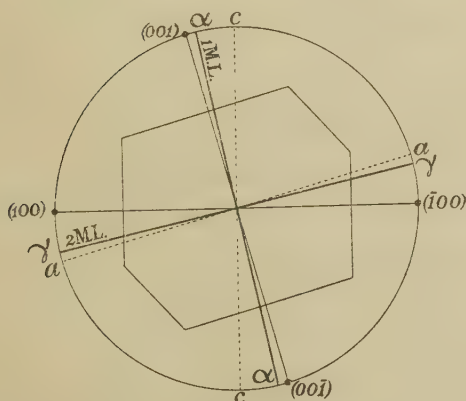


FIG. 9.

behind the normal to $c\{001\}$. As the latter is $15^{\circ} 30'$ in front of the vertical axis c , this extinction direction, which is the first median line, lies $12^{\circ} 32'$ in front of the vertical axis c . The second median line lies $2^{\circ} 58'$ above the inclined axis a . Topsøe obtained $12^{\circ} 20'$ and $3^{\circ} 12'$ for these two extinction angles. These facts are graphically illustrated in fig. 9.

Optic Axial Angle.—The results for 2E and for $2H_a$, $2H_o$, and the

true angle $2V_a$, from three pairs of plates, ground perpendicular to the two bisectrices, are given in the next two tables.

Apparent Optic Axial Angle in Air, 2E, of AmCu Selenate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean 2E.
Li.....	91 37	92 1	91 47	91 48
C.....	91 26	91 49	91 45	91 40
Na.....	90 42	90 57	90 51	90 50
Tl.....	89 45	89 51	89 58	89 51
Cd.....	89 20	89 32	89 13	89 22
F.....	88 51	88 50	88 39	88 47

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed 2H _a .	No. of plate perp. 2 M.L.	Observed 2H _a .	Calculated 2V _a .	Mean 2V _a .
Li.....	{ 1	51 12	1a	109 36	55 44	55 45
	{ 2	51 18	2a	109 52	55 44	
	{ 3	51 15	3a	109 35	55 48	
C.....	{ 1	51 6	1a	109 35	55 40	55 42
	{ 2	51 14	2a	109 51	55 42	
	{ 3	51 10	3a	109 33	55 44	
Na.....	{ 1	50 26	1a	109 30	55 6	55 7
	{ 2	50 30	2a	109 41	55 6	
	{ 3	50 29	3a	109 24	55 10	
Tl.....	{ 1	49 42	1a	109 25	54 29	54 31
	{ 2	49 45	2a	109 27	54 31	
	{ 3	49 42	3a	109 9	54 34	
Cd.....	{ 1	49 17	1a	109 19	54 9	54 10
	{ 2	49 17	2a	109 18	54 9	
	{ 3	49 15	3a	109 3	54 12	
F.....	{ 1	48 47	1a	109 14	53 44	53 48
	{ 2	48 54	2a	109 10	53 51	
	{ 3	48 47	3a	108 51	53 50	

Topsøe and Christiansen obtained $91^\circ 6'$ for 2E and $55^\circ 24'$ for $2V_a$, for sodium light.

Dispersion of the Median Lines.—This is very small and was determined by immersion in methyl salicylate, the refractive index for which is close to the mean index for the crystals. The median lines are dispersed $7'$ in the symmetry plane, so that the first median line is nearer to the vertical axis c for red C light than for green cadmium light, by this amount.

Effect of Temperature on Optic Axial Angle.—The angle in air 2E increased 8° on raising the temperature of the section-plate gradually from the ordinary temperature (14°) to 70° C.

Refractive Indices.—The results with the usual six 60° -prisms, each giving two indices, next follow.

Refractive Indices of Ammonium Copper Selenate.

Light.	α .	β .	γ .
Li.....	1·5161	1·5304	1·5347
C.....	1·5166	1·5309	1·5352
Na.....	1·5201	1·5344	1·5387
Tl.....	1·5235	1·5379	1·5423
Cd.....	1·5256	1·5402	1·5446
F.....	1·5278	1·5424	1·5469
G.....	1·5342	1·5488	1·5534

Mean of α , β , and γ for Na light = 1·5311.

α = Vibration direction parallel to first median line, $12^\circ 32'$ in front of vertical axis c .

β = " " " symmetry axis b .

γ = " " " second median line, $2^\circ 58'$ above inclined axis a .

Double refraction, $N_{\alpha\gamma-\alpha}$ = 0·0186.

General formula for β , corrected to a vacuum :—

$$\beta = 1.5134 + \frac{886\ 160}{\lambda^2} - \frac{4\ 974\ 300\ 000\ 000}{\lambda^4} + \dots$$

The α indices are equally well reproduced by the formula if the constant 1·5134 be diminished by 0·0144, and the γ indices if it be increased by 0·0043.

Observations at 70° indicated that the refractive indices of ammonium copper selenate diminish by about 0·0018 for a rise of temperature of 60° .

Topsøe and Christiansen obtained for β the values 1·5317, 1·5355, and 1·5437 for C, D, and F light respectively; and indirectly for α and γ , for sodium D light only, 1·5213 and 1·5395.

Axial Ratios of the Optical Ellipsoid.—

$$\alpha : \beta : \gamma = 0.9907 : 1 : 1.0028, \quad \alpha : b : c = 1.0094 : 1 : 0.9972.$$

Molecular Optical Constants.

	Axis of optical indicatrix.	α .	β .	γ .
Lorenz	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n \dots \dots$ { C	0·1360	0·1392	0·1401
	G	0·1399	0·1431	0·1440
	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m \dots$ { C	66·71	68·25	68·71
	G	68·60	70·16	70·65
	Specific dispersion, $n_G - n_C \dots \dots \dots$	0·0039	0·0039	0·0039
Gladstone ...	Molecular dispersion, $m_G - m_C \dots \dots \dots$	1·89	1·91	1·94
	Molecular refraction, $\frac{n-1}{d} M \dots \dots \dots$ C	113·98	117·14	118·09

Mean molecular refraction (Gladstone), $\frac{1}{3} (\alpha + \beta + \gamma) = 116·40$.

Comparison of Results.

Habit.—The crystals of the potassium, rubidium, and caesium salts of this large double selenate and double sulphate series of isomorphous salts have throughout been shown to exhibit characteristic habits of a very

definite kind, and in this copper group the three specific types are clearly exhibited. They are formed by the relative development of the basal pinakoid $c\{001\}$ and clinodomal prism $q\{011\}$, the former largely predominating in the potassium salt and the latter in the caesium salt, while in the rubidium salt the two forms are more or less equally developed, the habit of this salt being thus very clearly of intermediate character. The crystals of the ammonium salt are usually very much like those of the intermediate rubidium salt, but the limits are wider, the type shown by the potassium salt being also frequently approached in different individuals, and the caesium salt type more rarely.

Crystal Elements and Angles.—

Comparison of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	β .	$a : b : c$
Potassium copper selenate	103° 25'	0·7508 : 1 : 0·5143
Rubidium " "	104° 44'	0·7495 : 1 : 0·5066
Ammonium " "	105° 30'	0·7476 : 1 : 0·5150
Cæsium " "	105° 42'	0·7398 : 1 : 0·4981

The monoclinic axial angle β for rubidium copper selenate is thus approximately the mean of the corresponding axial angles for the potassium and caesium salts. The axial angle of ammonium copper selenate is nearly identical with that of caesium copper selenate.

The morphological axial ratios of the rubidium salt are likewise intermediate between the analogous ratios for the potassium and caesium salts.* The axial ratios of the ammonium salt are close enough to those of all three alkali metallic salts to indicate true isomorphism.

From the comparative Table on the next page, of 38 measured angles, the salient fact is derived that the whole of the angles of the rubidium salt are intermediate between those of the potassium and caesium salts (except pp' for which the angle remains identical).

Analysis of the Table shows that the average and maximum changes of angle are twice as great when potassium is replaced by caesium, as they are when potassium is replaced by rubidium. The average and maximum changes of interfacial angle are thus directly proportional to the change in atomic weight or atomic number.

* Thus both as regards the axial angle and the axial ratios the constants follow the order of the atomic weights and atomic numbers of the alkali metals present.

Atomic weights :— K = 38·85,	Rb = 84·9,	Cs = 131·9.
Atomic numbers :—K = 19,	Rb = 37	Cs = 55.

Comparison of the Interfacial Angles.

Angle.	KCu selenate.	RbCu selenate.	CsCu selenate.	AmCu selenate.
$\left\{ \begin{array}{l} ac = (100) : (001) \\ as = (100) : (101) \\ sc = (101) : (001) \\ cr' = (001) : (201) \\ cs' = (001) : (101) \\ s's' = (\bar{1}01) : (201) \\ s'a = (201) : (100) \end{array} \right.$	$\begin{array}{l} 76^\circ 35' \\ 46^\circ 42' \\ 29^\circ 53' \\ 62^\circ 55' \\ 38^\circ 24' \\ 24^\circ 31' \\ 40^\circ 30' \end{array}$	$\begin{array}{l} 75^\circ 16' \\ 46^\circ 5' \\ 29^\circ 11' \\ 63^\circ 25' \\ 38^\circ 21' \\ 25^\circ 4' \\ 41^\circ 19' \end{array}$	$\begin{array}{l} 74^\circ 18' \\ 45^\circ 43' \\ 28^\circ 35' \\ 63^\circ 37' \\ 38^\circ 9' \\ 25^\circ 28' \\ 42^\circ 5' \end{array}$	$\begin{array}{l} 74^\circ 30' \\ 45^\circ 13' \\ 29^\circ 17' \\ 64^\circ 34' \\ 39^\circ 9' \\ 25^\circ 25' \\ 40^\circ 56' \end{array}$
$\left\{ \begin{array}{l} ap = (100) : (110) \\ pp' = (110) : (120) \\ p'b = (120) : (010) \\ pp'' = (110) : (130) \\ p''b = (130) : (010) \\ pb = (110) : (010) \end{array} \right.$	$\begin{array}{l} 36^\circ 7' \\ 19^\circ 28' \\ 34^\circ 25' \\ 29^\circ 20' \\ 24^\circ 33' \\ 53^\circ 53' \end{array}$	$\begin{array}{l} 35^\circ 56' \\ 19^\circ 28' \\ 34^\circ 36' \\ 29^\circ 22' \\ 24^\circ 42' \\ 54^\circ 4' \end{array}$	$\begin{array}{l} 35^\circ 37' \\ 19^\circ 28' \\ 34^\circ 55' \\ 29^\circ 26' \\ 24^\circ 57' \\ 54^\circ 23' \end{array}$	$\begin{array}{l} 35^\circ 46' \\ 19^\circ 28' \\ 34^\circ 46' \\ 29^\circ 24' \\ 24^\circ 50' \\ 54^\circ 14' \end{array}$
$\left\{ \begin{array}{l} cq = (001) : (011) \\ qb = (011) : (010) \end{array} \right.$	$\begin{array}{l} 26^\circ 35' \\ 63^\circ 25' \end{array}$	$\begin{array}{l} 26^\circ 6' \\ 63^\circ 54' \end{array}$	$\begin{array}{l} 25^\circ 37' \\ 64^\circ 23' \end{array}$	$\begin{array}{l} 26^\circ 24' \\ 63^\circ 36' \end{array}$
$\left\{ \begin{array}{l} ao = (100) : (111) \\ oq = (111) : (011) \\ aq = (100) : (011) \\ qo' = (011) : (\bar{1}11) \\ o'a = (\bar{1}11) : (100) \end{array} \right.$	$\begin{array}{l} 50^\circ 2' \\ 28^\circ 0' \\ 78^\circ 2' \\ 34^\circ 29' \\ 67^\circ 29' \end{array}$	$\begin{array}{l} 49^\circ 20' \\ 27^\circ 28' \\ 76^\circ 48' \\ 34^\circ 28' \\ 68^\circ 44' \end{array}$	$\begin{array}{l} 48^\circ 53' \\ 27^\circ 0' \\ 75^\circ 53' \\ 34^\circ 27' \\ 69^\circ 40' \end{array}$	$\begin{array}{l} 48^\circ 35' \\ 27^\circ 34' \\ 76^\circ 9' \\ 35^\circ 7' \\ 68^\circ 44' \end{array}$
$\left\{ \begin{array}{l} co = (001) : (111) \\ op = (111) : (110) \\ cp = (001) : (110) \\ po' = (110) : (11\bar{1}) \\ o'c = (11\bar{1}) : (00\bar{1}) \end{array} \right.$	$\begin{array}{l} 35^\circ 43' \\ 43^\circ 29' \\ 79^\circ 12' \\ 56^\circ 3' \\ 44^\circ 45' \end{array}$	$\begin{array}{l} 34^\circ 54' \\ 43^\circ 13' \\ 78^\circ 7' \\ 57^\circ 16' \\ 44^\circ 37' \end{array}$	$\begin{array}{l} 34^\circ 11' \\ 43^\circ 5' \\ 77^\circ 16' \\ 58^\circ 16' \\ 44^\circ 28' \end{array}$	$\begin{array}{l} 35^\circ 0' \\ 42^\circ 29' \\ 77^\circ 29' \\ 57^\circ 4' \\ 45^\circ 27' \end{array}$
$\left\{ \begin{array}{l} bo = (010) : (111) \\ os = (111) : (101) \end{array} \right.$	$\begin{array}{l} 69^\circ 29' \\ 20^\circ 31' \end{array}$	$\begin{array}{l} 69^\circ 57' \\ 20^\circ 3' \end{array}$	$\begin{array}{l} 70^\circ 23' \\ 19^\circ 37' \end{array}$	$\begin{array}{l} 69^\circ 55' \\ 20^\circ 5' \end{array}$
$\left\{ \begin{array}{l} bo' = (010) : (\bar{1}11) \\ o's' = (\bar{1}11) : (101) \end{array} \right.$	$\begin{array}{l} 65^\circ 0' \\ 25^\circ 0' \end{array}$	$\begin{array}{l} 65^\circ 6' \\ 24^\circ 54' \end{array}$	$\begin{array}{l} 65^\circ 17' \\ 24^\circ 43' \end{array}$	$\begin{array}{l} 64^\circ 15' \\ 25^\circ 15' \end{array}$
$\left\{ \begin{array}{l} sq = (101) : (011) \\ qp = (011) : (110) \\ ps = (110) : (10\bar{1}) \end{array} \right.$	$\begin{array}{l} 39^\circ 10' \\ 84^\circ 29' \\ 56^\circ 21' \end{array}$	$\begin{array}{l} 38^\circ 22' \\ 85^\circ 48' \\ 55^\circ 50' \end{array}$	$\begin{array}{l} 37^\circ 38' \\ 86^\circ 57' \\ 55^\circ 25' \end{array}$	$\begin{array}{l} 38^\circ 38' \\ 86^\circ 14' \\ 55^\circ 8' \end{array}$
$\left\{ \begin{array}{l} s'q = (\bar{1}01) : (011) \\ qp = (011) : (110) \\ ps' = (110) : (10\bar{1}) \end{array} \right.$	$\begin{array}{l} 45^\circ 30' \\ 64^\circ 27' \\ 70^\circ 3' \end{array}$	$\begin{array}{l} 45^\circ 14' \\ 63^\circ 42' \\ 71^\circ 4' \end{array}$	$\begin{array}{l} 44^\circ 50' \\ 63^\circ 15' \\ 71^\circ 55' \end{array}$	$\begin{array}{l} 46^\circ 0' \\ 63^\circ 0' \\ 71^\circ 0' \end{array}$
$\left\{ \begin{array}{l} r'o' = (201) : (\bar{1}11) \\ o'p = (\bar{1}11) : (110) \\ pr' = (110) : (20\bar{1}) \end{array} \right.$	$\begin{array}{l} 34^\circ 27' \\ 93^\circ 27' \\ 52^\circ 6' \end{array}$	$\begin{array}{l} 34^\circ 45' \\ 92^\circ 42' \\ 52^\circ 33' \end{array}$	$\begin{array}{l} 34^\circ 54' \\ 92^\circ 13' \\ 52^\circ 53' \end{array}$	$\begin{array}{l} 35^\circ 14' \\ 92^\circ 34' \\ 52^\circ 12' \end{array}$

Replacement.	Average change. (Mean change of 38 angles.)	Maximum change.
K by Rb	33'	79' = 1° 19'
K by Cs	61'	148' = 2° 28'
K by NH ₄	47'	125' = 2° 5'

The average and maximum changes of angle occurring when ammonium is introduced instead of potassium are seen to be intermediate between the amounts caused by introducing rubidium and caesium respectively.

In 33 of the 38 compared angles, the change on replacing potassium by ammonium is in the same direction as when potassium is replaced by

rubidium or cæsium; of these 33 angles, 24 show larger changes than for the rubidium replacement, and in 10 of the whole 38 compared angles the change is greater even than when cæsium is introduced instead of potassium. The largest (absolute maximum) change of angle for the whole group of four salts is $2\frac{1}{2}^{\circ}$ ($2^{\circ} 28'$), which occurs in the case of one angle, $qp = (011):(\bar{1}10)$, when potassium in potassium copper selenate is replaced by cæsium, or *vice versa*. This angle also showed the maximum change of $2^{\circ} 16'$ in the cobalt group.

On comparing the table of crystal-angles for this group with that of the other groups studied, it is observed that the absolute values of the angles are generally distinctly different, often to the extent of half a degree, and occasionally by a whole degree. In this the copper group shows its individuality. Yet the relations between the values for the four salts are exactly those exhibited by the other groups. Hence the results for the copper group are particularly valuable.

Volume Constants.—

Volume Constants of the Copper Group of Double Selenates.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
KCu selenate	532·32	2·539	209·66	$\chi : \psi : \omega$ 6·1819 : 8·2338 : 4·2347
RbCu "	624·42	2·839	219·94	6·3179 : 8·4295 : 4·2704
CsCu "	718·42	3·073	233·79	6·4378 : 8·7022 : 4·3346
NH ₄ Cu "	490·48	2·223	220·64	6·2868 : 8·4093 : 4·3308

The density increases with the molecular weight, the changes for the respective replacements of K by Rb and Rb by Cs being as 5:4, the effect thus diminishing as the mass grows. The ammonium salt is naturally much the lightest member of the group.

The molecular volume of the three alkali metallic salts increases at an accelerating rate, as the atomic weight or atomic number rises, the amount for the two changes of metal being 10·28 and 13·85 respectively. The molecular volume of ammonium copper selenate is close to (0·7 higher than) that of rubidium copper selenate, a result as regards the ammonium and rubidium salts which has always been observed throughout the series.

There is naturally an increase in the molecular volume on replacing sulphur (atomic number 16) by selenium (atomic number 34), and as there are two atoms of sulphur or selenium in the molecule of the double salt, we obtain the increase *per* atom by subtracting the molecular volume of the double sulphate from that of the double selenate and dividing by two. The results of this operation, for the analogous salts of all the six pairs of

groups of monoclinic double salts yet completely investigated, are given in the next Table. The results per atom for the simple sulphates and selenates are also added for comparison.

Increase of Molecular Volume on Replacing S by Se.

Salt group.	Increase per atom.
Copper	6·6 to 7·3 units.
Cobalt	6·3 to 6·7 "
Iron	6·2 "
Nickel	6·1 to 6·8 "
Magnesium	6·0 to 6·1 "
Zinc	6·3 to 6·4 "
Simple salts of alkalis	6·5 to 6·8 "

The copper group here again shows its individuality by affording a somewhat higher range of change in the molecular volume than is exhibited in the other groups.

The molecular distance (topic axial) ratios of the rubidium salt are intermediate between those for the potassium and cæsium salts, the axial or edge dimensions of the monoclinic elementary cell of the space-lattice thus increasing progressively with the atomic weight or atomic number of the alkali metal. These constants for the ammonium salt are similar to those for the rubidium salt, two of the three dimensions being slightly less, and the third somewhat greater, the balance corresponding to the very slight increase in the molecular volume of the ammonium salt as compared with that containing rubidium.

Cleavage.—There is a perfect cleavage parallel to the orthopinakoid $r'\{\bar{2}01\}$ in the crystals of all four salts. This is the common cleavage direction of the whole series of double sulphates and selenates. In addition, however, all four salts of this copper group have been observed to cleave with considerable facility parallel to the clinopinakoid $b\{010\}$.

Orientation of Optical Ellipsoid.—The position of the ellipsoid is conveniently determined by giving the position for a specific wave-length of that one of its two rectangular axes lying in the symmetry plane which is not far removed from the vertical crystal axis c ; it is the α axis of the indicatrix for all the salts, and the first median line for the potassium and ammonium salts, but the second median line for the rubidium and cæsium salts.

Inclination of α Axis of Indicatrix to Vertical Axis c , in front, for Na Light.

NH ₄ Cu selenate	12° 32'
KCu "	13° 34'
RbCu "	23° 5'
CsCu "	37° 12'

Thus in the crystals of the salts containing the three alkali metals the ellipsoid is situated so that this axis α is further and further removed from the vertical axis as the atomic weight or atomic number of the alkali metal increases. The ellipsoid thus rotates about the fixed symmetry axis b when one alkali metal is exchanged for another, and progressively at an accelerating rate, following the ascending order of the atomic weights or atomic numbers

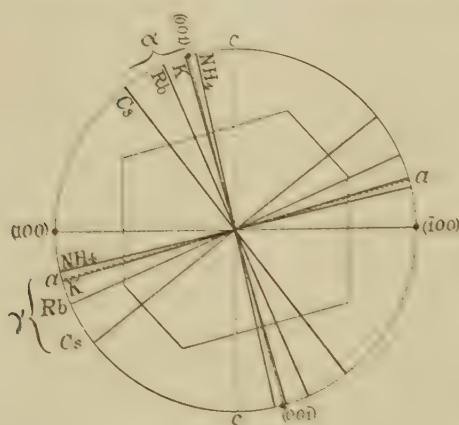


FIG. 10.

of the interchanged metals. In the case of the ammonium salt the position of this axis α is a degree nearer to the vertical axis c than for the potassium salt. Its position for each of the four salts now under consideration is graphically indicated in fig. 10, which shows the progression in the case of the metallic salts very clearly.

The positions of the α axis are more forwards than for the other groups, a fact also shown by the copper double sulphates. The

progressive relations are, however, the same.

Optic Axial Angles.—The plane of symmetry $b\{010\}$ is the common plane of the optic axes for the whole group. In the cases of the rubidium and caesium salts the sign of the double refraction is positive, and the first median line is the γ axis of the indicatrix lying in the symmetry plane not very far removed from the inclined crystal axis a . In the cases of the potassium and ammonium salts, however, the double refraction is negative, which is uncommon in the series, and the first median line is the α axis of the indicatrix, lying very close to the normal to $c\{001\}$.

Optic Axial Angles $2V_a$ of the Copper Group of Double Selenates.

	KCu selenate.	AmCu selenate.	RbCu selenate.	CsCu selenate.
Li.....	88° 49'	55° 45'	52° 57'	48° 20'
C.....	88 46	55 42	52 58	48 20
Na.....	88 27	55 7	53 11	48 26
Tl.....	88 3	54 31	53 26	48 33
Cd.....	87 55	54 10	53 35	48 37
F.....	87 36	53 48	53 43	48 42

The optic axial angle is thus seen to decrease with the atomic weight or atomic number of the alkali metal, the value for the rubidium salt being intermediate, but much nearer to that of the caesium salt. The optic axial

angle of ammonium copper selenate comes between those for the potassium and rubidium salts, and quite close to that of the latter salt.

Refractive Indices.—

Comparison of the Refractive Indices.

Index.	Light.	KCu selenate.	RbCu selenate.	NH ₄ Cu selenate.	CsCu selenate.
α	Li	1·5063	1·5117	1·5161	1·5243
	C	1·5068	1·5122	1·5166	1·5248
	Na	1·5101	1·5153	1·5201	1·5282
	Tl	1·5132	1·5185	1·5235	1·5316
	Cd	1·5150	1·5204	1·5256	1·5335
	F	1·5171	1·5225	1·5278	1·5355
	G	1·5230	1·5284	1·5342	1·5416
β	Li	1·5190	1·5146	1·5304	1·5259
	C	1·5195	1·5152	1·5309	1·5264
	Na	1·5228	1·5183	1·5344	1·5298
	Tl	1·5266	1·5216	1·5379	1·5332
	Cd	1·5286	1·5237	1·5402	1·5352
	F	1·5308	1·5257	1·5424	1·5372
	G	1·5368	1·5317	1·5488	1·5434
γ	Li	1·5312	1·5280	1·5347	1·5355
	C	1·5317	1·5286	1·5352	1·5360
	Na	1·5349	1·5318	1·5387	1·5394
	Tl	1·5386	1·5354	1·5423	1·5427
	Cd	1·5406	1·5375	1·5446	1·5447
	F	1·5428	1·5396	1·5469	1·5467
	G	1·5491	1·5461	1·5534	1·5530
Mean refractive index $\frac{1}{3}(\alpha + \beta + \gamma)$ for Na light		1·5226	1·5218	1·5311	1·5325
Double refraction, Na _{$\gamma-\alpha$}		0·0248	0·0165	0·0186	0·0112

The refractive indices have throughout the series exhibited a progressive increase, as potassium is replaced by rubidium, and the latter in turn by cæsium, the last-mentioned change being the greater. In several of the groups, however, the oppositely progressive effect of the diminution of double refraction has more than neutralised the progression in refractive index as regards the maximum index γ in the case of the rubidium salt, so that this index for the rubidium salt has been rendered slightly lower than that for the potassium salt. In this copper group the effect is further aided by the fact that the sign of the double refraction is by exception negative in the potassium salt, while positive as usual in the series for the rubidium and cæsium salts; the intermediate β index of the rubidium salt is thus very close to the minimum index α of that salt, while in the case of the potassium salt the β index is nearer to the γ index, as required by negative double refraction. Moreover, as the optic axial angle of the rubidium salt is very small, the indices α and β are quite exceptionally close together. All these effects combine not only to neutralise the usual progression in

refractive index, but actually to render the β and γ indices of the rubidium salt less than those for the potassium salt. The progression is clearly apparent, however, when the cæsium salt is reached.

In this copper group also, the refractive indices of the ammonium salt are nearer to those of the cæsium salt than usual, and owing to the ammonium salt being negative in double refraction, and with a very small optic axial angle which brings the β indices very close to the γ indices, the β indices of the ammonium salt are even somewhat larger than those of the cæsium salt.

In these exceptional facts the copper group again shows its individuality, quite subsidiary phenomena affecting the usual clear progression.

Double Refraction.—The usual marked diminishing progression, with atomic weight or atomic number of the alkali metal, which has been observed throughout the series as regards double refraction, $\text{Na}_{\gamma-\alpha}$, is very clearly exhibited by the copper group. The value for the ammonium salt is intermediate between the values for the potassium and rubidium salts, whereas for the other groups it has lain between the rubidium and cæsium salt values. In all these properties, however, the ammonium salt behaves exactly in accordance with the assumption that it is a member of the isomorphous group, the values being very similar to those for the alkali metallic salts.

Axial Ratios of the Optical Indicatrix.—The second set on the right in the Table, in which the total change in the dimensions of each of the three axes of the optical indicatrix (ellipsoid) is expressed, on passing from one salt to another, exhibits clearly the facts referred to under the heading of Refractive Indices. These ratios are directly proportional to the refractive index, and for the second set the β value for the potassium salt is taken as unit for all four salts.

Axial Ratios of the Optical Indicatrix.

			$\alpha : \beta : \gamma$	$\alpha : \beta : \gamma$
KCu	selenate		0·9917 : 1 : 1·0080	0·9917 : 1 : 1·0080
RbCu	„		0·9980 : 1 : 1·0089	0·9951 : 0·9971 : 1·0059
NH ₄ Cu	„		0·9907 : 1 : 1·0028	0·9982 : 1·0076 : 1·0104
CsCu	„		0·9990 : 1 : 1·0063	1·0036 : 1·0046 : 1·0109

Molecular Optical Constants.—

Specific Refraction and Dispersion (Lorenz).

Selenate.	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = n_s$						Specific dispersion. $n_g - n_c$		
	For ray C(H α).			For ray H γ near G.					
	α .	β .	γ .	α .	β .	γ .	α .	β .	γ .
AmCu ...	0·1360	0·1392	0·1401	0·1399	0·1431	0·1440	0·0039	0·0039	0·0039
KCu	0·1172	0·1196	0·1220	0·1203	0·1230	0·1253	0·0031	0·0034	9·0033
RbCu	0·1057	0·1063	0·1086	0·1085	0·1091	0·1116	0·0028	0·0028	0·0030
CsCu	0·0997	0·0999	0·1015	0·1024	0·1026	0·1041	0·0027	0·0027	0·0026

Molecular Refraction and Dispersion (Lorenz).

Selenate.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$						Molecular dispersion. $m_g - m_c$		
	For ray C(H α).			For ray H γ near G.					
	α .	β .	γ .	α .	β .	γ .	α .	β .	γ .
KCu	62·37	63·69	64·94	64·05	65·46	66·70	1·68	1·77	1·76
RbCu	66·02	66·35	67·79	67·77	68·12	69·66	1·75	1·77	1·87
AmCu	66·71	68·25	68·71	68·60	70·16	70·65	1·89	1·91	1·94
CsCu	71·62	71·81	72·90	73·53	73·74	74·81	1·91	1·93	1·91

Molecular Refraction (Gladstone and Dale).

Selenate.	$\frac{n-1}{d} M$ for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha + \beta + \gamma)$.
	α .	β .	γ .	
KCu	106·26	108·92	111·48	108·89
RbCu	112·65	113·32	116·26	114·08
AmCu	113·98	117·14	118·09	116·40
CsCu	122·69	123·07	125·31	123·69

The whole of the specific and molecular optical constants of the rubidium salt are intermediate between those of the potassium and caesium salts. The very important constant molecular refraction thus shows clearly the real progression in refractive power which accompanies the change in the atomic weight or atomic number of the interchangeable alkali metals, being removed from the disturbing causes referred to under the heading Refractive Indices. The change is an accelerating one, the difference between the values for the rubidium and caesium salts being greater than that between the potassium and rubidium salts.

The conclusion is independent of temperature, similar effects being observed for change of temperature with both density and refractive index.

The molecular refraction of ammonium copper selenate is not far removed from that of the rubidium salt, although the slight difference (on the higher side) in the case of the β axis of the indicatrix is somewhat greater in this copper group than has usually been observed throughout the series, owing to the two salts being of opposite signs of double refraction, which separates unduly the β values (on opposite sides of the mean between α and γ).

On comparing these values of the molecular refraction for the copper group of double selenates with the analogous copper double sulphates, it is found that the selenate values are higher by 6.4 to 8.3 Lorenz units, or 11.3 to 14.6 Gladstone units. Dividing by two, the number of sulphur or selenium atoms present in the molecule, this gives 3.2 to 4.2 Lorenz units, or 5.7 to 7.3 Gladstone units, for the increase per atom, when sulphur is replaced by the heavier selenium.

The following Table shows how this accords with similar results from the other groups of salts studied.

Increase of Molecular Refraction on Replacing S by Se.

Salt group.	Lorenz units.	Gladstone units.
Copper	3.2-4.2	5.7-7.3
Cobalt	3.5-4.1	6.5-7.1
Iron	3.5-4.0	6.4-7.1
Nickel	3.5-4.0	6.3-7.2
Magnesium	3.4-3.6	6.3-6.7
Zinc	3.5-3.7	6.5-6.9
Simple salts of alkalies	3.4-3.8	6.2-7.2

The copper group again distinguishes itself by a greater wideness between the limits. The mean result is about the same, however, as for the other groups studied.

Concluding Remarks.

The general results for this copper group of double selenates confirm those previously established for the magnesium, zinc, iron, nickel, and cobalt groups, and for all the analogous double sulphates, and in a peculiarly valuable manner. For it has been shown with regard to most of the crystallographic (morphological and physical) properties dealt with, that the absolute values of the constants expressing them are considerably different from those for the other groups (in this respect resembling the results for the copper group of double sulphates), and yet the relationships are remarkably similar. The same progression according to the atomic weight or atomic number of the interchangeable alkali metals, potassium, rubidium, and caesium, which by their interchange give rise to three of the four salts, is exhibited with respect to every property. And the similarity of the fourth

salt of the group, that of the radicle base ammonium, to the rubidium salt, in regard to molecular volume and the constants involving it—the topic axial (molecular distance) ratios and the molecular refraction—again indicates the closeness to isostructure of the crystals of the ammonium and rubidium salts.

The further progress made since the author's last memoir (on the cobalt group *loc. cit.*), on the structure of the atom, and the further elucidation of the real meaning of Moseley's law which has followed therefrom, have but further confirmed and explained the fact that the author's results are the natural consequence of that law, and of the progressive constructive complexity of the atoms of the elements which by their interchange give rise to the isomorphous series.

The author's next communication will include the description of the manganese and cadmium groups of double selenates, and will form the concluding memoir of this long series of investigations, which will have included 75 salts, and it will mark the completion of the extensive research which the author proposed to himself and commenced in the year 1890.

Arc Spectra in vacuo and Spark Spectra in Helium of Various Elements.

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[PLATE 1.]

I. *Introduction.*

The rapid progress in recent years in the investigation of arcing voltages and resonance potentials in metallic vapours and in their relation to certain spectral series, which for many elements lie in the extreme ultra-violet region of the spectrum, makes it of great importance to obtain as extensive and as accurate as possible a knowledge of the ultra-violet spectra of the elements. A stimulus has been given to this work by the recent research of Foote, Roguley, and Mohler,* on the ionisation potential of thallium vapour, and by that of Mohler, Foote, and Stinson,† on the ionisation potential of lead vapour. The series indicated by their values lie

* Foote, Roguley, and Mohler, 'Phys. Rev.,' vol. 13, January (1919).

† Mohler, Foote, and Stinson, 'Phys. Rev.,' vol. 14, December (1919).

almost entirely in the Schumann region, which can be studied only with the fluorite spectrograph or the vacuum grating spectrograph.

The present work is a continuation of that already carried out by McLennan, Ainslie, and Fuller,* on the vacuum arc spectra of various metals, and includes a study of the vacuum arc spectra of antimony, bismuth, calcium, magnesium, selenium, copper, and silver, and the spark in helium spectra of aluminium, antimony, bismuth, cadmium, calcium, lead, magnesium, thallium, and tin. The study of these spectra has been successful in that certain additions to our knowledge of the spectra of these elements has been made in every case.

II. *Apparatus.*

The spark spectra, and all but one arc spectrum, were taken on the fluorite spectrograph described by McLennan, Ainslie, and Fuller.†

The experimental details were the same as they employed. In all cases the instrument was washed with hydrogen before commencing an exposure, in order to insure a good vacuum and to remove the last traces of air. It was comparatively easy to obtain the hard X-ray vacuum, as indicated by the green fluorescence of a Geissler discharge tube attached to the spectrograph, using only the oil-sealed mechanical Trimount pumps.

The arc chamber or "lamp" is shown in fig. 1, and was found to be uniformly regular in operation. It consisted essentially of a cylindrical brass vessel enclosed in a larger brass one, so that a water cooling system could be used with the more intense arcs. From the bottom and the side projected two arms through which the electrodes passed, the apertures being made air-tight by means of oil seals and stuffing-boxes. In this way the electrodes could be advanced or withdrawn without impairing the vacuum. The leads to the electrodes were insulated from the case by porcelain bushings at the electrode end, and ebonite at the exterior end. The arc was, through all the experiments, entirely controlled by hand.

The light for the spectrograph was taken out of the side of the arcing chamber at right angles to the plane containing the electrodes, and a window on the opposite side provided for observation of the arc.

With substances having a high melting point, such as copper, calcium, and silver, the metal in rod form was attached directly to the leads. The metals of lower melting point were placed in hollow steel electrodes, and the arc chamber rotated through 45° , so that the melted metal would not run out. It was found that the steel did not enter into the arc. The connection between the arcing chamber and the spectroscope was made by a conical brass sleeve

* McLennan, Ainslie, and Fuller, 'Roy. Soc. Proc.,' A, vol. 95 (1919).

† *Ibid.*

the actual joint being made air-tight with a covering of thick-walled pure gum rubber tubing. This was found to give the desired flexibility at this union.

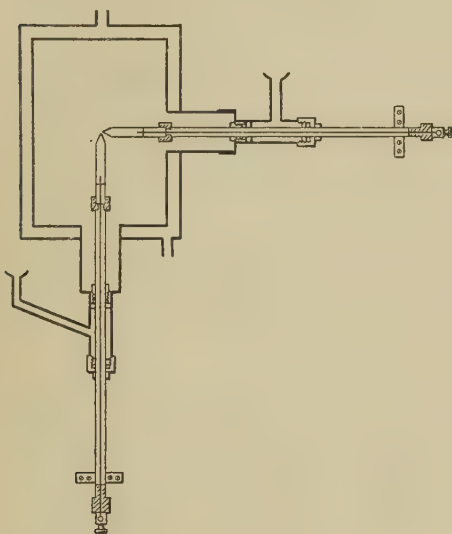


FIG. 1.

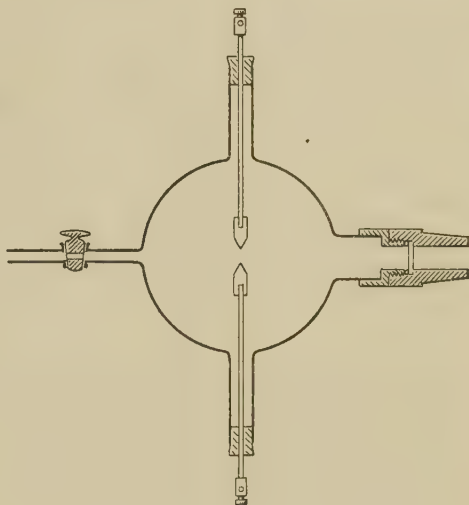


FIG. 2.

In studying spark spectra it was decided, since a supply of helium was available, to use that gas as the atmosphere surrounding the spark. Its transparency to ultra-violet light is well known as a result of Lyman's work,* and the fact that its spectrum in the region λ 2300 Å.U. to λ 1400 Å.U. is extremely meagre, made it especially suitable for such work. The spark chamber used is shown in fig. 2. It consisted essentially of a glass bulb with two side tubes and a well-ground glass tap. Two steel electrodes, having at their tips the metal to be studied, were inserted into the spark chamber through rubber stoppers, which were firmly fitted into the side tubes. A conical brass fitting, closed with a fluorite window, was waxed on to the large side tube. It was found that this arrangement provided an air-tight chamber and yet allowed ready adjustment of the electrodes when they become too widely separated. The distance between the spark gap and the fluorite window was about 8 cm.

To fill the bulb with helium it was connected in series with two cocoanut charcoal tubes to the Trimount pumps. The whole was thoroughly evacuated, the charcoal tubes being heated during the pumping, before the liquid air was applied to them. In this way an extremely hard vacuum was obtainable in the bulb. The helium was then permitted to enter through the two

* Lyman, 'Spectroscopy of the Extreme Ultra-violet.'

cocoanut charcoal tubes in liquid air until atmospheric pressure was reached. The tap was then turned off and the apparatus was ready for use. As the helium available had already been purified to approximately 98 per cent. purity, it is thought that the gas admitted to the bulb must have been of very high purity.

As it was found that a Clapp-Eastham transformer generating 10,000 volts was insufficient to give more than a weak spark, other arrangements had to be devised. A quite satisfactory method was to join the terminals of a 20-inch induction coil to a spark gap in air and to the inside coatings of two Leyden jars. The outside coatings of these jars were joined to the electrodes of the spark chamber. In this way a heavy discharge could be obtained when the spark in air was $1\frac{1}{2}$ –2 inches between spheres of $1\frac{1}{2}$ cm. in diameter.

III. *Method of Determining Wave-lengths.*

In calculating the wave-lengths of the lines of the spectra, the method of hyperbolic interpolation by means of a Hartmann dispersion formula was used. The standard lines employed were obtained from Eder and Valenta's Atlas, Lyman's measurement of the aluminium spark, and the measurement of the arc spectra of carbon, tin and lead as found by McLennan, Ainslie, and Fuller. Schumann plates, prepared by the Adam Hilger Co., were used throughout in recording the spectra. The plates were measured with a Toepler comparator, and the average of results from several plates was used

Calibration Wave-Lengths.

Source.	Wave-length Å.U.	Observer.
Pb	2203·68	E. and V.*
Cd	2144·44	"
Al	1989·9	L.†
Al	1930·5	"
C	1930·5	McL., A. and F.‡
Sn	1899·8	"
Al	1854·7	L.
Al	1761·9	"
Al	1670·6	"
C	1656·9	McL., A. and F.
Al	1611·8	L.
Al	1605·6	"
Pb	1555·8	McL., A. and F.
Sn	1475·2	"
C	1464·5	"
Pb	1434·0	"

* Eder and Valenta, 'Atlas Typischer Spectren.'

† Lyman, 'The Spectroscopy of the Extreme Ultra-violet.'

‡ McLennan, Ainslie and Fuller, 'Roy. Soc. Proc.,' A, vol. 95 (1919).

in each case in the final calculation. The three lines used as the basis of the dispersion formula were chosen each time to suit the range of spectrum to be calculated.

In view of the comparatively small dispersion of the spectrograph, and the combined error of the standard lines and the dispersion formula, a greater accuracy than 0.5 Å.U. cannot be claimed for all the measurements, though in the region of shorter wave-lengths where the dispersion is greater the error is possibly as small as 0.3 Å.U.

IV. Results.

1. *Antimony*.—The most recent work on the antimony arc is that of Takamine and Nitta,* who measured its spectrum as far as $\lambda 1858.0$ Å.U. in both arc and spark. The spectrum has been extended to about $\lambda 1450$ Å.U. In the experiments a fairly steady arc, *in vacuo*, was obtained by putting chemically pure antimony in steel electrodes, and using a current of from 5–6 ampères at 110 volts. As shown in Table I, the spectrum contained several fairly strong lines in the region below $\lambda 1850$ Å.U. and extended well down to $\lambda 1400$ Å.U. For convenience in reference the antimony spark spectrum is included in the same Table as the results obtained by Takamine and Nitta and Bloch.† It will be noted that in the region covered by other observers the agreement is fairly good, though all their lines have not been recorded, and for this reason have been omitted from the Table.

2. *Bismuth*.—The bismuth arc was obtained by using chemically pure bismuth metal in steel electrodes, a bright intermittent arc being struck with from 5–10 ampères at 200 volts. In Table II are given the results of the bismuth arc and spark spectra, together with the measurements of the bismuth spark, by MM. L. et E. Bloch.‡ Although in the present work many of their lines are missing, the agreement of those obtained is quite good. The spectrum has been extended to about $\lambda 1435$ Å.U.

3. *Calcium*.—For the calcium arc rod electrodes cut from larger pieces were used, thus obviating the necessity for the steel cups. With a current of from 10–15 ampères at 200 volts a very brilliant and steady arc was easily produced. It was found that the calcium metal was not rapidly used up in the arc, and repeated exposures could be taken without replacing the electrodes. For purposes of comparison, included in Table III are the values

* Takamine and Nitta, 'Memoirs of the College of Science,' Kyoto Imperial University, vol. 2, No. 2 (1917).

† Bloch, 'Journal de Physique,' 4, August–September, 1914.

‡ MM. L. et E. Bloch, 'C. R.,' No. 6, vol. 170, 1920.

Table I.—Antimony.

Authors.				Takamine and Nitta.		Bloch.
Arc Å.U.	Int.	Spark Å.U.	Int.	Arc Å.U.	Spark Å.U.	Spark Å.U.
1931·0	5	1930·8	2	1931·1	1931·1	1930·83
1926·6	5	1926·6	1	1926·6	1926·6	1926·61
—	—	1922·6	4	—	1922·6	1922·68
1899·2	3	—	—	1899·7	1899·7	—
1890·5	3	1891·0	2	1891·3	1891·3	—
1882·1	4	1882·5	2	—	1882·6	—
—	—	1878·1	2	—	1878·1	1877·91
1870·7	10	1870·8	10	1870·4	1870·4	1870·58
1867·8	8	—	—	1867·3	1867·3	—
—	—	1839·1	4	—	—	—
1829·4	5	—	—	—	—	—
1814·2	6	1814·3	2	—	—	—
1810·2	5	1810·1	2	—	—	—
1799·9	5	1800·0	2	—	—	—
1788·0	2	1788·1	1	—	—	—
1780·6	4	1780·5	2	—	—	—
1762·6	10	1762·3	10	—	—	—
1735·9	5	—	—	—	—	—
—	—	1730·7	7	—	—	—
—	—	1725·3	7	—	—	—
—	—	1717·1	2	—	—	—
—	—	1712·0	9	—	—	—
1702·3	4	—	—	—	—	—
1699·0	4	—	—	—	—	—
—	—	1678·1	2	—	—	—
—	—	1674·2	7	—	—	—
—	—	1667·2	3	—	—	—
1640·8	3	—	—	—	—	—
—	—	1635·0	2	—	—	—
1631·5	2	—	—	—	—	—
1613·9	1	—	—	—	—	—
1607·5	4	1607·7	1	—	—	—
1600·6	4	1601·0	8	—	—	—
1585·2	5	1585·4	8	—	—	—
1574·9	2	—	—	—	—	—
1566·1	4	1566·3	8	—	—	—
1554·6	2	1554·7	2	—	—	—
1540·7	2	1540·7	2	—	—	—
1535·8	2	—	—	—	—	—
1533·5	4	—	—	—	—	—
1514·1	7	1514·1	4	—	—	—
—	—	1506·4	3	—	—	—
1504·9	6	1504·8	2	—	—	—
1499·2	7	1500·3	3	—	—	—
1495·6	4	—	—	—	—	—
1493·3	4	—	—	—	—	—
1438·7	4	—	—	—	—	—
1437·0	7	—	—	—	—	—

found by Saunders* in the arc and spark, and also those of Eder and Valenta.† The strong doublet has been found to exist in the arc at

* Saunders, 'Astrophys. Jl.,' vol. 33, No. 3, 1916.

† Eder and Valenta, *loc. cit.*

Table II.—Bismuth.

Authors.			Bloch.	
Arc Å.U.	Int.	Spark Å.U.	Int.	Spark Å.U.
1902·6	10	1902·6	10	—
1823·3	5	1823·6	8	1823·5
—	—	—	—	1811·1
—	—	—	—	1796·2
1791·5	7	1791·5	7	1791·8
1787·1	4	1787·3	7	1787·0
1776·7	5	1776·7	7	1776·7
—	—	—	—	1757·9
—	—	—	—	1749·7
—	—	—	—	1682·2
—	—	—	—	1671·0
1611·7	2	1611·5	2	1611·4
—	—	1609·9	2	1609·6
—	—	1606·6	1	1606·3
—	—	1601·6	2	1601·4
1592·1	2	1592·0	2	1591·7
—	—	1574·1	1	1573·9
—	—	1564·1	1	1564·0
—	—	—	—	1553·3
1538·7	2	1538·3	1	1538·5
—	—	1537·0	1	1537·3
1533·7	6	1533·7	3	1533·7
1521·3	1	—	—	1521·2
—	—	—	—	1503·5
1497·6	2	—	—	—
1462·5	1	—	—	—
1455·4	5	—	—	—
1436·8	4	—	—	—

λ 1555·1 Å.U. and λ 1553·5 Å.U. It will be noted that there is a marked similarity between the arc and spark spectra of this element.

Attempts were made to photograph the strontium and barium arc spectra by using the fused chloride in carbon electrodes, but with little success. The last lines recorded in strontium was the doublet λ 2165·99 Å.U. and λ 2152·91 Å.U., and in barium the doublet λ 2335·27 Å.U. and λ 2304·36 Å.U.

4. *Magnesium*.—Owing to the noticeable difference between the values obtained for the magnesium in hydrogen by Lyman,* and for the spark in air by Handke,† it seemed of some importance to remeasure the spectrum of this element as given by the arc *in vacuo* and by the spark in helium. The results are in close agreement with those of Lyman, with the exception that the line λ 1828·1 Å.U. is recorded only in the arc spectrum and not in the spark at all. Handke does not record this line in the spark, but his other

* Lyman, *loc. cit.*

† Handke, *loc. cit.*

Table III.—Calcium.

Authors.			Saunders.		Eder and Valenta.
Arc Å.U.	Int.	Spark Å.U.	Int.	Arc Å.U.	Spark Å.U.
—	—	—	—	2211·86	—
2209·0	6	2209·0	8	—	2208·95
2198·0	5	2198·0	6	—	2198·03
—	—	—	—	2187·66	—
—	—	—	—	2179·44	—
—	—	2176·4	1	—	—
—	—	—	—	2167·57	—
—	—	2152·9	1	—	—
2132·0	1	2132·0	1	2132·51	—
2113·9	8	2113·9	10	—	2113·01
2103·6	7	2103·6	8	—	2103·47
—	—	—	—	2088·14	—
—	—	—	—	2083·38	—
—	—	—	—	2073·26	—
2070·4	2	—	—	—	—
—	—	—	—	2065·42	—
1851·2	1	—	—	—	—
1840·4	10	1840·4	10	1840·26	—
1838·2	10	1838·2	10	1838·13	—
1815·0	4	1815·0	4	—	—
1807·5	4	1807·5	4	—	—
—	—	1742·8	4	—	—
1680·5	2	—	—	—	—
1555·1	4	1555·1	3	—	—
1553·5	4	1553·5	3	—	—

values have not been confirmed. That the magnesium spectrum does contain a line at this wave-length has been amply established by the work of several observers of the arc spectrum. In our work the arc spectrum has been extended slightly. The results with comparison values are given in Table IV.

Table IV.—Magnesium.

Authors.				Lyman.
Arc Å.U.	Int.	Spark Å.U.	Int.	Spark Å.U.
2026·5	10	2026·5	10	—
1828·1	5	—	—	1828·1
1753·6	2	1753·6	5	1753·6
1750·7	1	1750·7	4	1750·9
1747·8	2	—	—	—
1743·0	1	—	—	—
1737·5	3	1737·7	6	1737·8
1734·3	2	1735·0	5	1735·0
1730·2	1	—	—	—
1706·8	1	—	—	—

5. *Selenium*.—The spectrum of selenium does not appear to have been studied hitherto in this region at all. The experimental details were quite simple. Powdered selenium metal was placed in hollow carbon electrodes in the arc chamber. When the arc was struck between the carbons the selenium boiled up through it and its spectrum was emitted. The carbon lines were eliminated by comparison photographs of the carbon arc alone. The spectrum was quite rich in lines well spread throughout the range of the spectrograph. The results are given in the following Table :—

Table V.—Selenium.

Authors.		Authors.		Authors.	
Arc Å.U.	Int.	Arc Å.U.	Int.	Arc Å.U.	Int.
2296·9	5	1854·4	5	1593·3	1
2164·3	6	1759·8	2	1587·7	1
2139·0	1	1751·2	1	1580·2	2
2074·8	8	1690·4	3	1532·3	1
2063·1	7	1674·9	3	1530·9	1
2040·0	8	1670·8	4	1501·9	1
1994·7	1	1626·2	1	1457·5	1
1959·7	4	1622·5	1	1448·1	2
1918·5	2	1621·3	2	1446·1	1
1913·0	2	1617·3	1	1436·8	3
1897·7	3	1610·8	1	1432·8	1
1857·9	4	1606·6	2		

6. *Silver*.—The vacuum arc was obtained by using electrodes of $\frac{1}{4}$ -inch pure silver rod. With a current of from 15–20 ampères at 200 volts a very steady and bright white arc could be maintained. The results are given in Table VI along with the corresponding values of the silver spark as recorded by MM. L. et E. Bloch* and Handke.† Apparently the spark spectrum is very much richer in lines than the arc spectrum.

7. *Copper*.—The copper vacuum arc spectrum has already been studied as far as λ 1400 Å.U. by McLennan, Ainslie, and Fuller,‡ but an extension of the work was attempted using the vacuum grating spectrograph developed by McLennan and Lang.§ The experimental arrangements were the same as employed by them. Pure copper rods, $\frac{1}{4}$ -inch in diameter, were used as electrodes in the arc “lamp,” and with a current of about 15 ampères at

* MM. L. et E. Bloch, *loc. cit.*

† Handke, ‘Inaug. Diss.’ Berlin, August, 1909.

‡ McLennan, Ainslie, and Fuller, *loc. cit.*

§ McLennan and Lang, ‘Roy. Soc. Proc.’ A, vol. 95, 1919.

Table VI.—Silver.

Authors.		Bloch.	Handke.
Arc Å.U.	Int.	Spark Å.U.	Spark Å.U.
1888·7	2	1888·82	1888·1
1879·3	2	1879·60	1879·0
1872·8	4	1872·66	1872·5
1866·9	4	1866·36	1867·1
1859·1	2	1859·88	1859·4
1855·7	1	1855·61	1855·3
1838·9	3	1839·2	1839·5
1828·3	4	1828·1	1828·6
1821·8	1	1822·2	1822·0
1816·1	4	1815·4	1816·4
1807·8	4	1807·5	1808·0
1801·4	1	1801·4	1802·1
1793·2	2	1793·1	1793·9
1768·2	1	—	1768·6
1750·5	10	1750·6	1751·3
1727·8	1	—	1727·2
1721·8	1	—	1722·4
1693·5	8	1693·4	1694·0
1680·8	2	1681·2	1681·4
1677·8	1	1678·5	1678·7
1674·0	3	1674·9	1674·5
1657·1	7	1657·4	
1650·8	1	1651·5	
1566·6	1	1566·3	
1561·7	8	1561·7	
1555·3	2	1555·2	
1540·1	2	1541·8	

200 volts, a bright intermittent arc was produced. With good vacuum conditions in the spectrograph an exposure of three hours was sufficient to produce a well-defined spectrogram. The spectrum has been extended to about λ 1216 Å.U. The results, together with the corresponding values of Eder and Valenta,* and Handke,† are given in Table VII.

8. *Aluminium*.—For purposes of calibration the aluminium spark in helium was photographed. Clear, sharply-defined spectrograms were obtained with exposures of about 10 minutes. As will be seen from the Table, no lines other than those given by Lyman,‡ were recorded on the plates. Four of his lines were not recorded on any of our plates. Three of his values were taken as the basis of the dispersion formula for this spectrum and, though our values are somewhat less throughout the whole range of spectrum, the discrepancies probably represent the error of the dispersion formula.

* Eder and Valenta, *loc. cit.*† Handke, *loc. cit.*‡ Lyman, *loc. cit.*

Table VII.—Copper.

Authors.		Eder and Valenta.	Handke.
Arc Å.U.	Int.	Spark Å.U.	Spark Å.U.
1999·7	10	1999·71	
1989·3	5	1989·20	
1979·3	7	1979·27	
1944·1	2	1944·11	
1840·6	4	—	1840·1
1783·7	1	—	1783·7
1768·6	2	—	1769·1
1750·2	5	—	1749·9
1741·2	4	—	1741·0
1728·1	1	—	1727·8
1722·2	5	—	1721·9
1711·4	1	—	1710·6
1708·9	4	—	1708·5
1705·3	3	—	1705·0
1702·6	3	—	1702·6
1686·9	2	—	1686·6
1684·7	2	—	1684·3
1681·7	2	—	1681·9
1679·1	2	—	1679·0
1674·4	2	—	1674·5
1671·7	2	—	1671·6
1670·0	2	—	1669·8
1658·4	2	—	1657·8
1654·4	2	—	1654·1
1652·0	2	—	1651·9
1642·1	5	—	1641·8
1639·0	1	—	1638·4
1628·1	2	—	1627·3
1626·1	2	—	1625·6
1616·7	2	—	1615·5
1613·5	2	—	—
1609·7	2	—	1608·8
1606·5	2	—	1606·1
1605·4	2	—	1605·4
1603·1	2	—	1602·9
1600·1	2	—	1600·0
1594·0	3	—	1594·2
1548·9	1		
1543·5	1		
1537·3	1		
1443·4	1		
1437·5	1		
1432·0	1		
1410·7	1		
1385·4	2		
1377·1	2		
1367·9	2		
1359·2	4		
1346·3	1		
1216·1	5		

9. *Cadmium*.—The cadmium spark has been measured by Saunders* and more recently by MM. L. et E. Bloch.† In the region to λ 1707·04 Å.U.

* Saunders, *loc. cit.*

† MM. L. et E. Bloch, *loc. cit.*

Table VIII.—Aluminium.

Authors.		Lyman.	Authors.		Lyman.
Spark Å.U.	Int.	Spark Å.U.	Spark Å.U.	Int.	Spark Å.U.
1989·9	9		1759·8	2	1760·0
1935·1	5		—	—	1751·7
1930·5	4		1749·8	1	1750·0
1862·6	10	1862·8	—	—	1747·7
1858·3	2	1858·2	1745·2	1	1745·3
1854·5	10	1854·7	1742·4	1	1742·7
1818·6	1	1818·5	1724·7	4	1725·0
1776·7	1	1776·9	1720·9	3	1721·2
—	—	1773·8	1719·0	2	1719·3
1767·4	2	1767·6	—	—	1718·3
1765·5	2	1765·7	1670·6	5	1670·6
1763·8	3	1763·8	1611·5	4	1611·8
1761·8	2	1761·9	1605·6	3	1605·6

our results are in quite good agreement with theirs, but below that, certain discrepancies occur between our results and those of Bloch, which are difficult to explain. There is apparently little similarity between the arc and spark spectra of this element, and for this reason values of the arc spectrum have not been included with the others in Table IX. The results show that a slight extension of the spark spectrum has been made.

Table IX.—Cadmium.

Authors.		Bloch.	Saunders.
Spark Å.U.	Int.	Spark Å.U.	Spark Å.U.
1844·6	10	1844·9	1844·68
1808·4	1	—	—
1793·2	5	1793·3	1793·06
1789·1	4	1789·0	1789·04
1781·0	2	—	—
1773·2	4	1773·1	1772·89
1769·0	4	1768·8	1768·54
1747·9	10	1747·7	1747·77
1721·8	5	1721·7	1721·76
1707·1	3	1707·2	1707·04
1678·3	1	1678·7	
1655·7	1	1656·1	
1651·8	1	1652·3	
1628·6	1	1628·5	
1605·8	1	1606·7	
1601·5	2	1601·5	
1568·3	1		
1560·9	1		

10. *Lead*.—The spark spectrum of the element does not seem to have been previously measured in the region below $\lambda 1850$ Å.U., although the arc spectrum has been measured by several observers. The present work has extended the spark spectrum to about $\lambda 1555$ Å.U. For reference the arc measurements of Saunders* are included in Table X, and it will be seen that our values are in good agreement with the corresponding lines in the arc.

Table X.—Lead.

Authors.		Saunders.	Authors.		Saunders.
Spark Å.U.	Int.	Arc Å.U.	Spark Å.U.	Int.	Arc Å.U.
2170·8	5	2170·60	—	—	1868·59
—	—	2112·37	1863·0	1	—
2060·9	4	—	1822·1	10	1822·06
—	—	2053·83	1796·3	10	1796·53
—	—	2022·64	1726·7	3	1726·71
1971·9	3	—	1710·8	3	—
1958·3	4	—	1682·0	7	1682·54
1904·8	4	1904·88	1671·3	7	—
1898·3	1	—	1554·8	3	—
1890·0	4	—	—	—	—

11. *Thallium*.—The spark spectrum of thallium has been measured to $\lambda 1814\cdot72$ Å.U. by Saunders,† but no other observations appear to have been made. The arc has been recently studied by McLennan, Ainslie, and Fuller‡ and a considerable extension of the spectrum made. In the present work it has been found that some similarity exists between the arc and spark spectra in the fluorite region, but in addition to their values we have recorded some five new lines in the region below $\lambda 1850$ Å.U. In Table XI are given the measurements along with those of other observers.

12. *Tin*.—Although the spark spectrum of tin has already been studied by Handke,§ and many lines recorded in the range of spectrum down to $\lambda 1700$ Å.U., it was thought worth while to make a remeasurement of it under the different conditions of our experiments. Surprisingly few lines were found on our plates compared with the number given by Handke. The arc spectrum is much richer in lines than the spark spectrum which seems somewhat unusual. Our values are a little lower than Handke's but are in good agreement with the arc lines of McLennan, Ainslie, and Fuller.|| The results are given in Table XII.

* Saunders, *loc. cit.*

† Saunders, *loc. cit.*

‡ McLennan, Ainslie, and Fuller, *loc. cit.*

§ Handke, *loc. cit.*

|| McLennan, Ainslie, and Fuller, *loc. cit.*

Table XI.—Thallium.

Authors.		Saunders.	McLennan, Ainslie and Fuller.
Spark Å.U.	Int.	Spark Å.U.	Arc Å.U.
1908·7	10	1908·68	1907·8
1892·7	10	1892·72	1891·8
1881·0	7	1881·19	—
1871·2	2	1871·47	—
1837·4	1	1837·96	—
1827·8	8	1828·00	1827·3
1814·6	10	1814·72	1814·2
1792·5	7		1792·2
1660·0	3		1660·0
—	—		1653·8
1597·0	1		—
1583·9	1		—
1572·3	2		—
1568·8	2		—
1561·8	3		1561·8
1558·9	3		1559·0
1538·4	2		1538·5
1508·0	2		1508·2
1506·6	2		—
1500·1	3		1499·8
1492·0	2		1491·0
1477·2	2		1478·0

Table XII.—Tin.

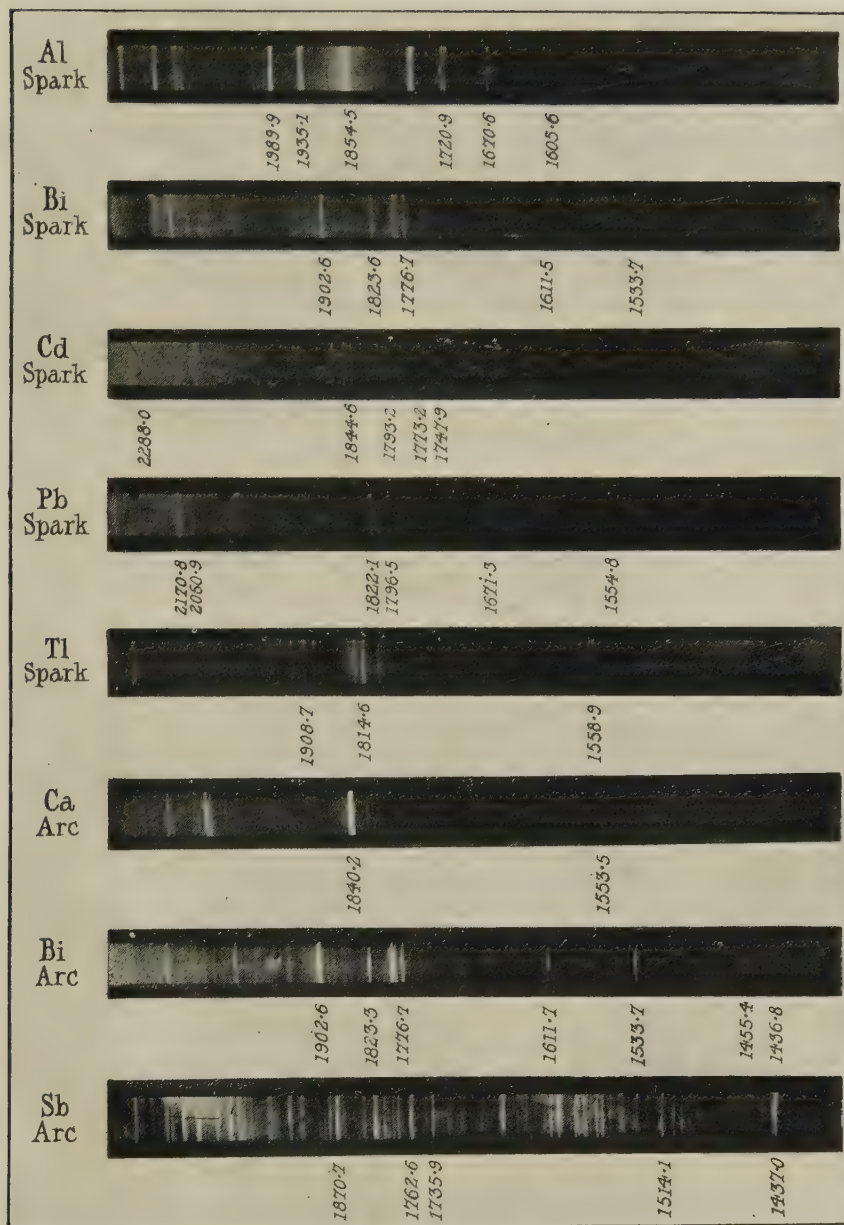
Authors.		Handke.	Authors.		Handke.
Spark Å.U.	Int.	Spark Å.U.	Spark Å.U.	Int.	Spark Å.U.
1899·8	10	1900·4	1757·3	5	1758·2
1831·1	3	1832·0	1699·2	1	1700·1
1811·0	8	1812·0	1475·2	1	

V. *Summary.*

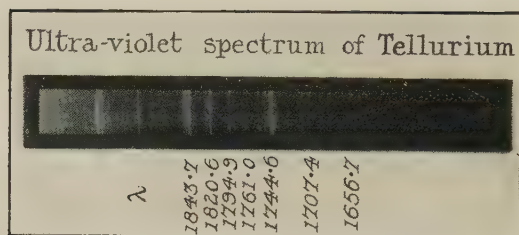
1. The vacuum arc spectra of antimony, bismuth, calcium, magnesium, selenium, silver, and copper, and the spark spectra in helium of antimony, bismuth, aluminium, cadmium, lead, magnesium, thallium, and tin, have been investigated in the region below λ 1850 Å.U.

2. The measurements of the arc spectra of antimony, bismuth, calcium, and selenium, and the spark spectra of antimony and lead, appear to be the first recorded for these substances in this region.

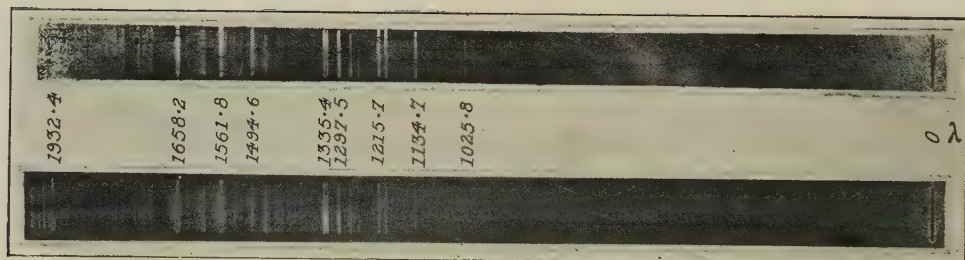
3. The work with the vacuum grating spectrograph has resulted in the extension of the vacuum arc spectrum of copper to about λ 1216 Å.U.



A



B



Spark Spectra of Various Elements in Helium in the Extreme Ultra-Violet.

By J. C. McLENNAN, F.R.S., Professor of Physics, University of Toronto,
and A. C. LEWIS, M.A.

(Received June 18, 1920.)

[PLATE 2, A.]

1. *Introduction.*—Although rapid progress has been made in recent years through the work of a number of investigators* in extending our knowledge of the spectra of many of the elements far into the extreme ultra-violet, there remains quite a number of the elements whose spectra in this region have not been examined.

Among those elements whose spectra in the extreme ultra-violet region have not been studied are silicon, tellurium, molybdenum and zirconium. The spectra of these elements have now been obtained by the writers, by the use of a spectrograph provided with a fluorite train, and the following paper contains an account of the investigation.

2. *Apparatus.*—The fluorite spectrograph used by McLennan, Ainslie, and Fuller† was used at the inception of the investigation, but it was soon found that it was not well designed for rapid work. The instrument was completely re-designed, and as re-modelled and constructed it is shown in fig. 1.

To avoid a great many sources of leak, and to give space for modifying the arrangement of the optical train, the prism, focussing lens and photographic plate-holder were inclosed in a cylindrical vessel, NM, made of cast bronze, of 1 cm. wall-thickness.

The vessel was 7.5 cm. deep and 30 cm. internal diameter. The lid, when in position, merely rested on the cylinder, and the junction was very carefully ground so that the application of a little "Airtite" was quite sufficient to hold an X-ray vacuum. The lid was removed when adjustment of the spectrograph was necessary and also when a photographic plate was

* Lyman, 'Ast. Phys. Jl.,' vol. 43, No. 2, March, 1916; Saunders, 'Ast. Phys. Jl.,' vol. 43, No. 3, April, 1916; Takamine and Nitta, 'Mem. of Coll. of Sci.,' Kyoto Imperial; S. Pina de Rubies, 'Inst. Nac. de Ciencias,' Madrid, 1917; McLennan, Ainslie, and Fuller, 'Roy. Soc. Proc.,' A, vol. 95, p. 316 (1919); McLennan and Lang, 'Roy. Soc. Proc.,' A, vol. 95, p. 258 (1919); L. and E. Bloch, 'Comptes Rendus,' No. 6 p. 320 (February 9, 1920).

† McLennan, Ainslie, and Fuller, *loc. cit.*

inserted. The plates used were $5'' \times 1''$, and were cut from Schumann plates prepared by the Adam Hilger Company.

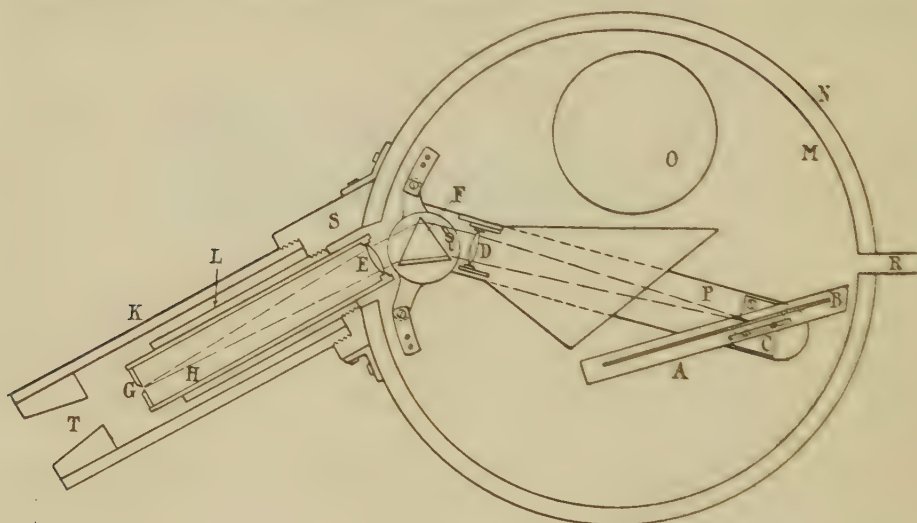


FIG. 1.

The prism, F, was placed on an adjustable platform near the wall of the chamber and an opening was made to allow the attachment of a collimator tube. A piece of cast bronze, S, was attached to the vessel at this point, and to this was attached the collimator tube, K, at an angle of 30° to the diameter of the vessel. Inside this tube and concentric with it was placed a tube, H, carrying the slit, G, and collimating lens, E, kept in position by sleeve, L. Openings were made in L and H to allow air to pass freely from the collimator tube to the cylindrical vessel. The collimator tube was terminated by an opening, T, very carefully ground so as to admit the spark chamber by the joint, E, shown in fig. 2. The platform on which the prism was mounted was clamped in position by two set-screws, as shown in the diagram. An arm, P, on which was mounted the photographic plate-holder, AB, and the focussing lens, D, was fixed so that it could be rotated through an angle about an axis through the centre of the prism. When the instrument was adjusted properly the arm could be clamped by a set-screw. The carrier for the focussing lens, D, and C, that for the plate-holder, AB, could be slid along the arm, and could be clamped by screws when in position. A feather-way was cut in the plate-holder to allow its being adjusted in a line parallel to itself. It was guided by two screws.

The instrument could be approximately adjusted by using the aluminium spark in air as a source of light, and $\lambda 1854 \text{ \AA.U.}$ could be easily focussed

visibly by using a fluorescent screen in AB. Further adjustments were made by taking a series of photographs of the spectra of aluminium and antimony sparks in helium. To remove the water vapour from the spectrograph, a cylindrical glass vessel, O, containing phosphorus pentoxide covered with glass-wool, was placed in the instrument as shown. The air was removed from the apparatus by means of a set of oil-sealed mechanical Trimount pumps. The connections were made with lead piping from the pumps to the aperture, R.

A short Geissler tube, to which was attached the terminals of a small 4-volt induction coil, served to show the degree of exhaustion in the apparatus. During exhaustion the instrument was washed with electrolytic hydrogen, and a vacuum which showed a greenish fluorescence in the Geissler tube could be obtained in a few minutes.

3. *Spark Chamber.*—The type of sparking chamber used is shown in fig. 2. It consisted of a glass bulb, approximately 10 cm. in diameter.

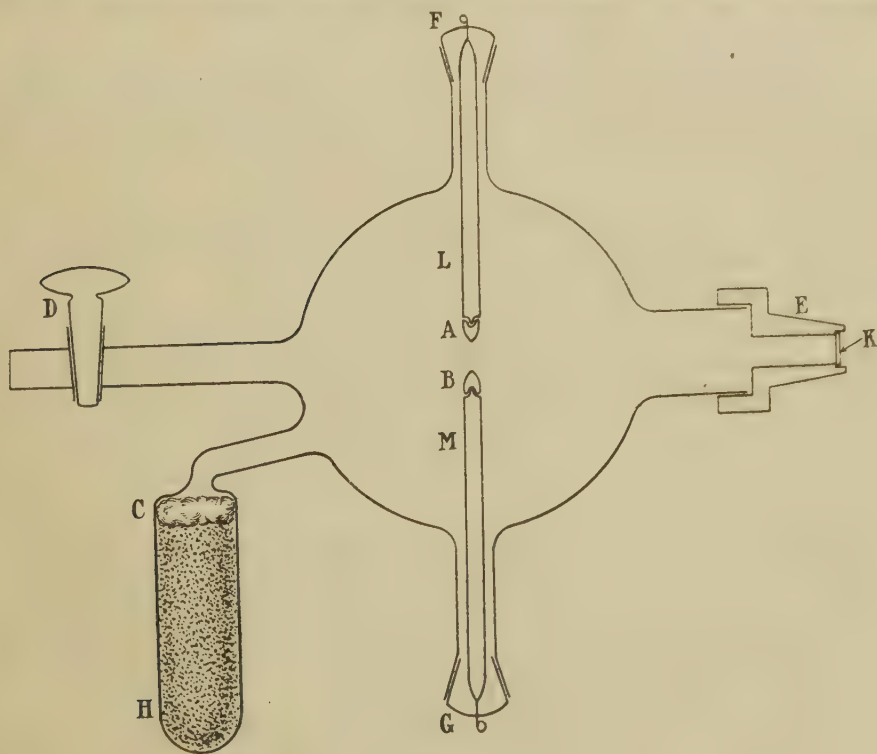


FIG. 2.

Aluminium rods, L, M, were sealed into ground-glass taps, F, G. The pieces of elements under experiment were connected at A, B. A brass carrier, E,

for carrying the fluorite window, K, was sealed with wax to the chamber. As shown in the diagram the brass carrier, E, was provided with a conical terminal with a well-ground surface. This terminal made a close fit with the matrix shown at the end of the collimator tube indicated in fig. 1, and when slightly smeared with "Airtite" it made a good seal.

Helium was used to fill the chamber at atmospheric pressure, and it was purified by passing it slowly through three tubes of carbon granules maintained at the temperature of liquid air. The gas was admitted by the tap, D, and during the experiment the side-tube, H, containing carbon granules covered with glass-wool, was maintained at liquid-air temperature to absorb any gases other than hydrogen that might be given off during the spark discharge.

As a filling for the fluorite spectrograph, helium possesses the advantage that, while it is perfectly transparent for radiations whose wave-lengths lie between $\lambda 1900 \text{ \AA.U.}$ and $\lambda 1250 \text{ \AA.U.}$, the radiation which it can be made to emit within these limits consists, in so far as is known, of but the single wave-length $\lambda 1640 \text{ \AA.U.}$

In making the experiments, the spark was obtained from the discharge of two $\frac{1}{2}$ -gallon and 1-gallon Leyden jars, charged with a 10-inch induction coil. The elements used were obtained from Messrs. Eimer and Amend, New York.

4. *Method of determining Wave-lengths.*—In calibrating the instrument, the spectrum of aluminium was used as a standard. Wave-lengths previously measured were selected, and the constants λ_0 , c and d_0 in a Hartmann dispersion formula $\lambda = \lambda_0 + c/d - d_0$ were calculated and used to compute the unknown wave-lengths. Superimposed on the spark spectra of the various elements in helium was the aluminium spark in air. This provided a known zero line and at the same time did not interfere with lines shorter than $\lambda 1854 \text{ \AA.U.}$ The plates were measured with an Otto Toepler and Son comparator.

5. *Results.*—The spectrum of silicon in the upper ultra-violet region had been investigated by Prof. McLennan and E. Edwards, with an optical system of quartz down to $\lambda 1842.2 \text{ \AA.U.}$ * Below this limit the only new wave-lengths observed in the present investigation with silicon appeared at $\lambda 1745 \text{ \AA.U.}$, $\lambda 1742.5 \text{ \AA.U.}$, and $\lambda 1657 \text{ \AA.U.}$

The spectra of tellurium, molybdenum and zirconium were examined with the results given in Table I, and these are considered to be about correct to $0.5 \text{ \AA.U.}$ It will be seen from the Table that a strong doublet appears common to all the spectra in the neighbourhood of $\lambda 1745 \text{ \AA.U.}$

* Prof. McLennan and Edwards, 'Phil. Mag.,' vol. 30, October, 1915.

Table I.

Tellurium.	Intensity.	Molybdenum.	Zirconium.
$\lambda = 1634 \cdot 4$	1		
1638 ·5	1		
1644 ·7	1		
1656 ·8	1	1652 ·7	
1662 ·5	1	1656 ·6	1656 ·7
1670 ·8	1		1670 ·3
1675 ·0	1	1672 ·4	
1677 ·7	1		
1682 ·5	1		
1688 ·1	1		
1699 ·3	1		
1707 ·4	2		
1712 ·3	2	1712 ·4	1712 ·3
1717 ·1	1		
1721 ·9	1		
1728 ·4	1		1725 ·1
			1729 ·8
1732 ·7	1	1731 ·9	
1742 ·3	5	1737 ·3	
1744 ·8	5	1742 ·2	1742 ·4
1748 ·3	1	1744 ·7	1745 ·0
1750 ·3	1	1749 ·3	
			1751 ·6
		1754 ·4	
1761 ·0	1	1759 ·7	
		1763 ·9	
1771 ·6	1	1767 ·0	
		1774 ·6	
1776 ·2	1		1775 ·1
1788 ·8	1	1789 ·0	
		1719 ·0	
1794 ·9	2		1793 ·1
		1809 ·7	
		1810 ·6	
		1813 ·6	1811 ·3
		1818 ·6	
1820 ·6	5	1820 ·8	
1826 ·7	1		
		1831 ·3	
1843 ·7	5	1843 ·2	1843 ·1
1848 ·7	3		
1851 ·4	3		
		1851 ·9	
		1854 ·0	1854 ·0

This Lyman gives as probably due to silicon.* A strong line at

* Lyman, 'Spectroscopy of the Extreme Ultra-violet,' p. 113.

$\lambda 1656.7 \text{ \AA.U.}$ was found on all the plates which Lyman gives as present in all metallic spark spectra in helium.* It was probably due to carbon from the decomposition of carbon monoxide given off from the wax joint.

As far as the writers can discover, none of the lines given for tellurium, molybdenum and zirconium have been measured hitherto for these elements. In the spectra of molybdenum and zirconium all the wave-lengths observed were of weak intensity. The radiations from tellurium, however, were stronger and their relative intensities are approximately those given in the Table. A reproduction of the spectrum of this element is given in Plate 2, A.

Note on Vacuum Grating Spectroscopy.

By J. C. McLENNAN, F.R.S., Professor of Physics, University of Toronto.

(Received July 7, 1920.)

[PLATE 2, B.]

I. Introduction.

In the spectroscopy of the extreme ultra-violet region, it is necessary to work either with arcs *in vacuo* or with sparks in one or other of the gases hydrogen or helium. As all other gases are opaque to ultra-violet radiations of short wave-length, their use is precluded. With many of the elements, arcs are difficult to maintain in a vacuum, and consequently one is driven to the use of sparks in either one or other of the two gases mentioned.

Lyman,† in his brilliant researches, has shown us that, with hydrogen, it is possible to obtain spectra extending to about $\lambda 900 \text{ \AA.U.}$ For radiations below this limit, it would appear, however, that hydrogen is more or less absorbing. With helium, on the other hand, the evidence available goes to show that this gas is transparent to radiations having wave-lengths as short as $\lambda 400 \text{ \AA.U.}$ or $\lambda 500 \text{ \AA.U.}$, and possibly shorter still. It would appear, then, that in the spectroscopy of the extreme ultra-violet, the procedure to be followed, which would permit of the most rapid progress being made, would be, in so far as the emission spectra are concerned, to work with a vacuum grating spectrograph, and to use an atmosphere of helium.

As regards the absorption spectra of the elements, helium also appears to be promising. From the work of Mackay and Ferguson,‡ it is known that arcs in helium can be struck and maintained for long periods between.

* Lyman, 'Spectroscopy of the Extreme Ultra-violet,' p. 124.

† Lyman, 'Ast. Phys. Jour.,' p. 100 (March, 1916).

‡ Mackay and Ferguson, 'Franklin Inst. Journ.,' p. 209 (February, 1916).

non-vapourising electrodes, such as those of tungsten. This means that, if a vacuum grating spectrograph, provided with a lamp of the "Pointolite" type, be filled with helium to a suitable pressure, arcs can be struck in the gas, when the requisite voltages are applied, which will provide a radiation consisting of wave-lengths extending probably to near $400 \lambda \text{ \AA.U.}$ From Lyman's experiments, it is known that radiations are given out by helium of approximately this wave-length, and can be recorded. With such a source of illumination available, it should be possible, by interposing the vapours of elements between the arc and the grating of the spectrograph, to obtain the absorption spectrum of the elements vapourised.

The experience of different workers in this field has shown that, for success, extreme precautions must be taken to ensure that the vacuum grating spectrograph is kept free of water vapour and all such gases as oxygen, nitrogen, carbon monoxide, etc.

This means, in the first place, that the vacuum grating spectrograph should be designed so as to be as free as possible from all liability to leaks, and, in the second place, provision should be made to remove any traces of oxygen, nitrogen, or carbon monoxide, which are liberated from the electrodes by the establishment of the arc, or which exude from the walls of the spectrograph after the instrument has been filled with helium and while exposures are being made.

A description has already been given of a vacuum grating spectrograph, which was used by the writer in collaboration with Mr. R. J. Lang,* for studying the vacuum arc spectra of a few of the elements. With this apparatus, it was found that, while the spectrum of carbon, for example, was recorded so far down as $\lambda 584 \text{ \AA.U.}$, it was only obtained when extreme care was taken to see that proper conditions obtained. Numerous difficulties and vexatious delays were experienced in making seals airtight and free from small leaks, chiefly because, in the design of the apparatus, a number of the seals were made between parts whose bearing surfaces were vertical. No provision was made in the apparatus, moreover, for removing exuded gases other than by pumping. The grating used, besides, was small, and this necessitated long exposures.

With a view to improving matters, the apparatus was redesigned, and provision was made not only for removing the exuded gases, but also for using a grating of any size, and for so arranging its carrier and its controls that adjustments could readily and easily be made. The description of this instrument follows:—

* McLennan and Lang, 'Roy. Soc. Proc.,' A, vol. 95, p. 258 (1919).

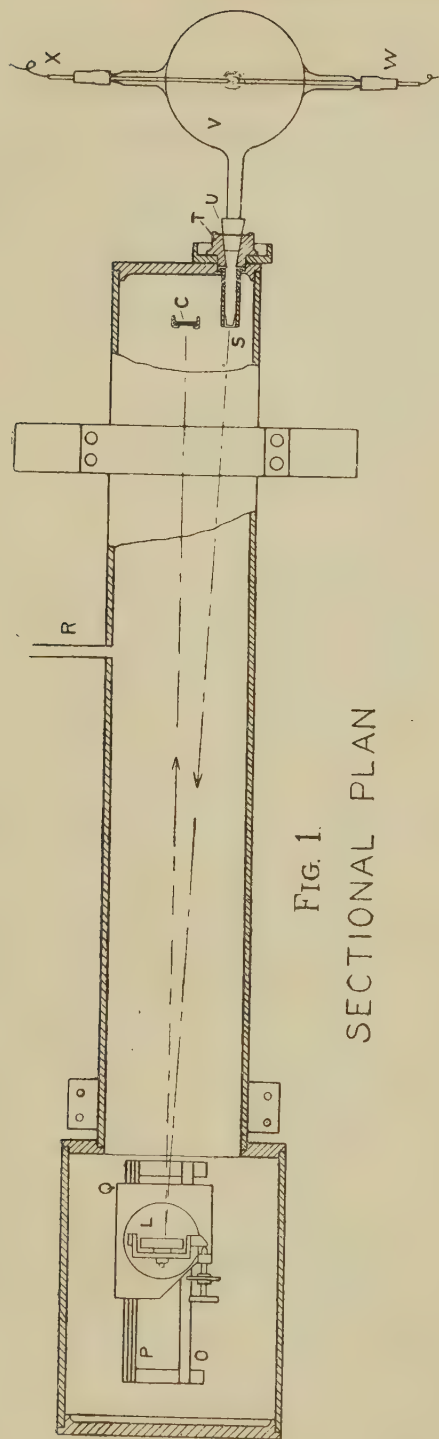


FIG. 1.
SECTIONAL PLAN

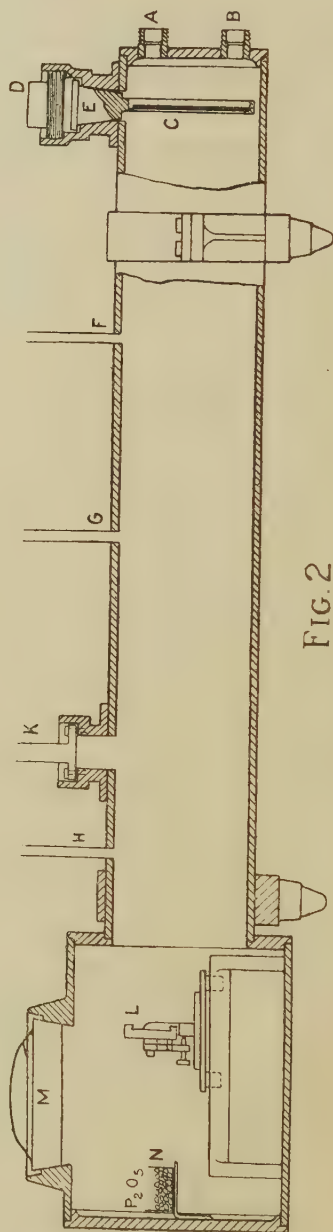


FIG. 2.
SECTIONAL ELEVATION

II. Vacuum Grating Spectrograph.

A sectional plan of the apparatus is shown in fig. 1 and a sectional elevation in fig. 2. Figs. 3, 4, and 5 show enlarged sketches of the horizontal and vertical sections, and of the end view of the plate holder, slit, and observation windows. The various parts of the apparatus are designated as follows :—

A and B—glass windows used for focusing and lining up spectra; C—photographic plate, Schumann sensitised; D—screw plug fitted with leather washer; E—support for plate, with ground joint; F, G, and H—leads to coconut charcoal tubes; K—vacuum pump connection bolted to tube body, with screws and leather gasket; L—ruled diffraction grating—6273 lines per centimetre, ruling 7.8 cm., and 1 metre radius; M—cap over opening (to adjust grating), with ground joint; N—lead box containing P_2O_5 covered with glass wool; O and P—rails for carriage; Q—carriage; R—lead to discharge tube; S—slit; T—bushing threaded externally, fitted with leather gasket. Female ground joint at centre; U—male member, ground joint, attached to light-source container; V—glass bulb 17 cm. in diameter, with two arms to support electrodes; W—pure gum rubber tubing slipped over arm of bulb and electrode; X—electrode; Y—sleeve carrying slit holder.

The spectrograph was designed for use with a grating having a radius of 1 metre, and it was therefore made about 130 cm. in length over all. The enlarged portion, which enclosed the grating, was 22 cm. in diameter and 30 cm. in length. The longer cylindrical portion of the apparatus had a diameter of 15 cm. As shown in the diagram, the opening above the grating was closed with a tinned

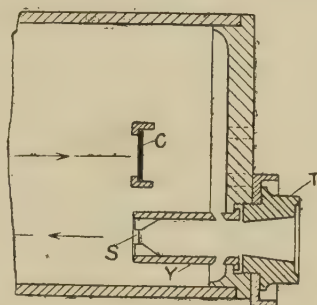


FIG. 3 HORIZONTAL SECTION

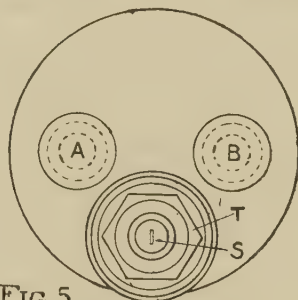


FIG. 5 END VIEW

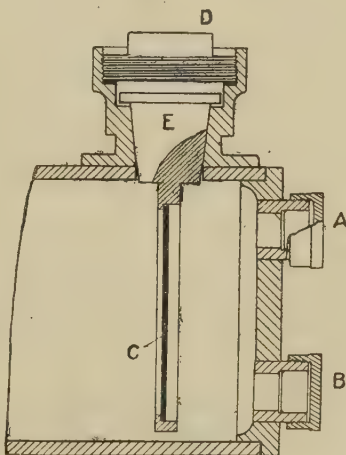


FIG. 4. VERTICAL SECTION.

brass cap, M, which fitted into a casting with a tapered ground joint. This opening gave ready access to the grating for adjustment, and, when the cap was placed in position, with its bearing surfaces slightly smeared with "Airtite," and the groove shown in the figure filled with melted wax, a perfect seal was obtained. The exhaust pipe, K, was joined to the apparatus as shown, so that the junction could be made absolutely airtight by flowing over it a small quantity of melted wax. It was arranged that the grating should be placed in position with its rulings horizontal. For some preliminary experiments, a grating was used, with a ruling 5.4 cm. wide and 7.8 cm. long, and having 6273 lines per centimetre. The mount was provided with rails, which allowed 15 cm. travel for the grating, and with the usual adjusting devices for orientating the grating in various ways.

The plate-holder, C, was suspended vertically and was attached to a conical plug, E, for support. This plug carried a guide for ensuring its being inserted correctly in position, and it was also provided with slits (not shown in the diagram), in which could be inserted two thin brass strips for screening off light from the photographic plate when the plate-holder was carried from and to the developing chamber.

When the plate-holder was in position, a threaded plug, D, provided with a leather washer, closed the opening, and an absolutely airtight joint was made by filling up with melted wax the groove made above the threaded portion of D. The glass windows at A and B were permanently fastened into the apparatus with sealing-wax and were used for observing the central image of the slit while adjusting the grating. These windows were provided with removable caps for cutting off extraneous light while exposures were being made. The slit, S, was carried by a sleeve, which could be inserted, rotated, or removed at will. When the slit was properly adjusted, the bushing, T, was screwed in and permanently sealed to the apparatus with hard wax. The brass tubes, F, G, and H, led to three cocoanut charcoal tubes, which during exposures were immersed in liquid air. A fourth tube, R, led to a Geissler tube, which, when excited by a small induction coil, was used to make observations on the pressure of the gas in the spectrograph.

In operating, the spectrograph gases were removed by means of two Trimount oil-sealed pumps, in series, driven by individual motors. These pumps were found to be highly efficient, a green fluorescence vacuum being obtainable with them in about 15 minutes.

With the grating described above, it was found that in the first order the dispersion was such that a spectrum extending from $\lambda = 0 \text{ \AA.U.}$ to $\lambda = 2000 \text{ \AA.U.}$ covered about 5 inches of the photographic plate. It was possible, therefore, to make observation over this range with but a single setting.

In adjusting the grating and slit, a plate coated with anthracene was inserted in the plate-holder and the light from a spark between aluminium terminals was used for illumination. As the distance between the centres of the two observation windows was about 5 inches, the procedure followed was to adjust the grating so that the bright central image could be seen either through the lower or the upper window. When this condition obtained, the illumination of the anthracene screen by the wave-length $\lambda = 1854 \text{ \AA.U.}$ could also then be seen as well through the other window if the orientation of the grating was correct. Fine focussing of the spectrum could be made by moving the mount of the grating with an adjusting screw slightly forward or back on the rails.

III. *Observations.*

When it was seen that the spectrograph from a mechanical and an operating point of view was satisfactory, some preliminary experiments were made with a sparking chamber such as that shown in fig. 1. The lamp and spectrograph were highly exhausted, washed out several times with charcoal-purified helium, and finally filled with this gas. The gas inlet valve was then closed and the charcoal tubes, attached at F, G, and H, were immersed in liquid air to take up any oxygen, nitrogen, or carbon monoxide liberated from the electrodes or from the walls of the apparatus. In these preliminary experiments it was found that in the visible portion of the spectrum the helium lines came out with strong intensity. In the ultra-violet region, however, there appeared on the photographic plates a series of gas lines in addition to those which were known to be due to the metals used.

It was then decided to make a special study of the spectrum obtainable from an arc in helium between tungsten terminals, in order to pick out the lines which one could definitely ascribe to helium itself. For this purpose the lamp shown in fig. 6 was designed.

Connection between the lamp and the spectrograph was made by means of the brass piece, E, which was sealed to the lamp by means of Khotinsky wax. This piece, E, as shown, was provided with a tapered end, which fitted, after careful grinding, very closely into its corresponding bushing, T, attached to the spectrograph. This was the only joint in the apparatus requiring to be frequently broken where the bearing surfaces were not horizontal. It was found, however, on account of the surfaces being ground to a good fit, that a slight smearing of "Airtite" made a perfectly gas-tight union.

N and R were two beads of tungsten, carried by two slender tungsten rods, which were carried by wires sealed into the glass stoppers F and G. C, H' was a glass tube filled with cocoanut charcoal covered with a wad of glass-wool.

J was a coil of fine tungsten wire, which formed part of the heating circuit, O, J, P. In operating the lamp, both it and the spectrograph were filled with purified helium through the tap, D, to a pressure of from 30 cm. to 40 cm. of mercury. Liquid air was then placed about the charcoal tube, H', and about those attached to the spectrograph at F, G, and H, fig. 1. F, fig. 6, was joined to the positive terminal of a 110-volt D.C. circuit, and O to the negative terminal of the same circuit. The circuit included, of course, a variable

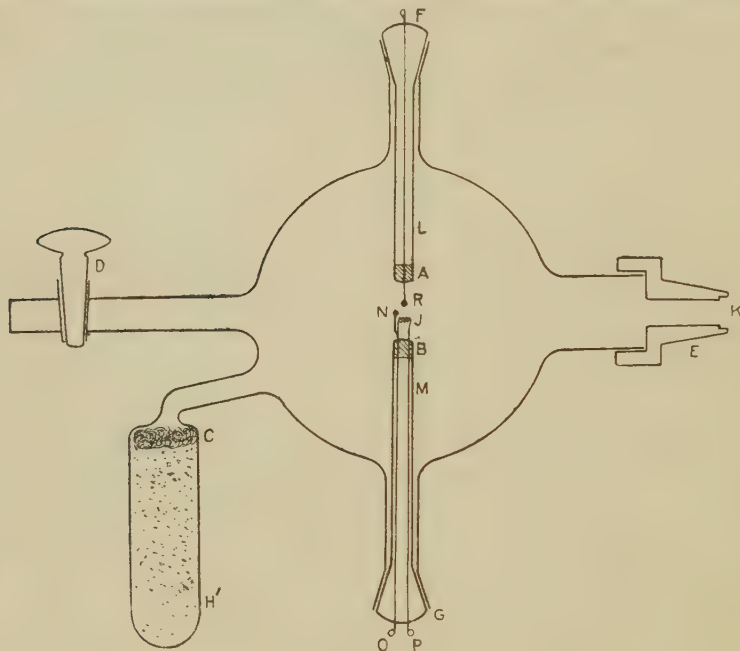


FIG. 6.

rheostat. The heating circuit, O, J, P, was provided with current from an insulated battery, and it was found that, at the pressures cited, as soon as J became incandescent the arc struck between J and R, and then finally between N and R. At this point the auxiliary heating battery was cut off and the arc persisted without it. At the pressures used, it was found quite easy to establish and maintain for hours arcs in helium with distances as great as 5 mm. or 6 mm. between the two tungsten beads, N and R. Tests made from time to time on these helium arcs showed a potential drop between the terminals of 45 volts when a current of 4.6 ampères was passing.

IV. Results.

A number of plates were taken of the spectra of the helium arcs established in the manner described, and all showed lines due to hydrogen

and possibly to carbon monoxide. A list of the wave-length determinations from measurements made on a number of plates is given in Table I, and a reproduction of the spectrum of the helium arc is shown in Plate 1. In the visible portion of the spectrum the helium lines came out with strong intensity.

Table I.—Helium Arc Spectrum.

Wave-length in Å.U.	Intensity.	Lyman's results.		Remarks.
		Wave-length in Å.U.	Origin suggested by Lyman.*	
1988·4	1			
1979·8	V.F.			
1975·6	V.F.			
1963·4	V.F.			
1952·1	1			
1932·4	15			
1921·3	V.F.	—	—	Due to carbon. McL., A. and F., 1930·5.† McL. and L., 1933·0.‡
1913·0	V.F.			
1904·0	1			
1884·2	1			
1875·2	1			
1863·3	3			
1855·0	1			
1848·7	V.F.			
1842·5	1			
1827·0	V.F.			
1812·6	V.F.	—	—	Carbon? McL., A. and F., 1811·9.
1795·9	1			
1786·9	V.F.	1785·1	CO?	
1777·3	1			
1754·0	1			
1745·6	4	—	—	Silicon?
1732·2	V.F.	$\left. \begin{array}{l} 1656·8 \\ 1633·7 \end{array} \right\}$	Uncertain— Strong in He discharge	Due to carbon. McL., A. and F., 1656·9.
1716·0	2			
1658·2	15			
1633·9	V.F.			
1601·9	1	1602·0	H	
1561·8	12	1561·2	H (Uncertain— Strong in He discharge)	Due to carbon. McL., A. and F., 1561·2.
1552·8	V.F.	1553·0	H	
1542·9	V.F.			
1534·4	V.F.	1535·0	H	
1516·4	V.F.	1516·4	H	
1506·8	V.F.	1506·6	H	
1494·6	9	1495·5	H	
1483·2	V.F.	1483·7	H	
1464·0	2	1463·9	H	
1412·4	V.F.	1413·0	H	
1358·2	V.F.	1358·2	H	
1335·4	14	1336·1	H	

* Lyman, "The Spectroscopy of the extreme Ultra-Violet," pp. 109–112, 124; 'The Ast. Phys. Jour.,' vol. 43, No. 2, p. 89 (1916); 'Proc. Amer. Acad. Arts and Sci.,' vol. 45, No. 10, March, 1910.

† McLennan, Ainslie, and Fuller, 'Roy. Soc. Proc.,' A, vol. 95, p. 316 (1919).

‡ McLennan and Lang, 'Roy. Soc. Proc.,' A, vol. 95, p. 358 (1919).

Table I—*continued*.

Wave-length in Å.U.	Intensity.	Lyman's results.		Remarks.
		Wave-length in Å.U.	Origin suggested by Lyman.*	
1329·0	13	1329·3	H	Uncertain origin.
1297·5	16	1297·4	H	
1277·6	4	1277·1	H	
1260·9	2	1261·9	H	
1242·7	1	1241·5	H	
1215·7	15	1216·0	H*	First members of Ritz series.
1199·7	13	1199·8	H or He	
1168·2	1	1169·2	H	
1151·9	1	1151·2	H	
1144·0	V.F.	1145·5	H	
1134·7	12	1134·7	H or He	
1085·1	1	1086·1	H or He†	
1037·3	2	1037·0	H or He	
1025·8	3	1026·0	H*	
				Second member of Ritz series.

* Lyman, 'Nature,' No. 2622, vol. 104, p. 565 (January 29, 1920).

† Lyman considers this line to be due to an impurity, 'Nature,' p. 565 (January 29, 1920).

An attempt was made to identify the wave-lengths, and suggestions as to their probable origin are given in the Table. Between $\lambda = 1000$ Å.U. and $\lambda = 1700$ Å.U., it would seem from Lyman's results that the majority of the wave-lengths was due to hydrogen. The two wave-lengths $\lambda = 1216$ Å.U. and $\lambda = 1026$ Å.U. constitute the first and second members of the principal series of the hydrogen spectrum predicted by Ritz, calculated by Bohr, and identified by Lyman. These, it will be seen, are among the more intense wave-lengths recorded. The wave-length $\lambda = 1329\cdot0$ Å.U. was among the strongest recorded, and appears to be of uncertain origin. Lyman gives a wave-length at $\lambda = 1329\cdot3$ Å.U. for hydrogen, but it appears to have come out on his plates with an intensity much less than it did on the plates obtained in this investigation. The wave-lengths $\lambda = 1561\cdot8$ Å.U., $\lambda = 1658\cdot2$ Å.U., and $\lambda = 1932\cdot4$ Å.U., are evidently due to carbon possibly having its origin in the tap grease used for making the joints gas-tight. For the range between $\lambda = 2000$ Å.U. and $\lambda = 1700$ Å.U., it will be seen that the spectrum consisted, with a few exceptions, of a series of wave-lengths of feeble intensity. These would not appear to have been due to hydrogen, but may have had their origin in the vapour of tungsten, which probably was present to a slight extent in the arcs. No indication was obtained of the presence of the wave-length $\lambda = 1640$ Å.U., which Lyman found could be obtained from helium. This was no doubt due to the fact that the arcing potential used in the experiments was only 45 volts.

An arcing potential of over 80 volts, on the Bohr theory, would be required to bring out this wave-length in the radiation emitted. The shortest wave-length recorded, it will be seen, came at $\lambda = 1025.8 \text{ \AA.U.}$, but, while this is so, it should be stated here that, on all the plates, indications were obtained of a faint continuous spectrum, extending to well below $\lambda = 500 \text{ \AA.U.}$ As the two tungsten beads, N and R, were highly incandescent during the operation of the arc, it may be that this continuous spectrum had its origin in the radiations emitted by them.

From the results of the investigation, it would appear that, in order to obtain the spectrum of helium in the extreme ultra-violet region with arcs between non-vapourisable electrodes, very special precautions will have to be taken to remove all traces of hydrogen from the helium in the spectrograph.

To do this, it would probably be necessary to admit small quantities of oxygen to the spectrograph from time to time, and to remove the excess oxygen by means of the charcoal tubes. It would probably prove more expeditious, however, to adopt a suggestion recently made by Lord Rayleigh, to cause the helium in the spectrograph to circulate in a closed cycle, part of the circuit being external to the spectrograph, and having included in it a tube, filled with charcoal, maintained at the temperature of liquid air, as well as others suitably equipped for getting rid of the hydrogen. Such a circulatory system could be operated for any time desired, and its use would enable one to raise the helium to the highest possible degree of purity.

The adoption of such special precautions to get rid of the hydrogen are all the more necessary if a pure spectrum of helium is to be obtained, for it has been shown that, in part of the ultra-violet region at least, the wave-lengths emitted by helium should be close to analogous ones emitted by hydrogen.

In view of the fact that the shortest wave-length recorded in this investigation was $\lambda = 1025.8 \text{ \AA.U.}$, it should be noted that the potential fall between the electrodes in the arc was only 45 volts. To bring out the shortest wave-lengths obtainable from helium, it would be necessary to arrange matters so that the drop in potential was considerably increased.

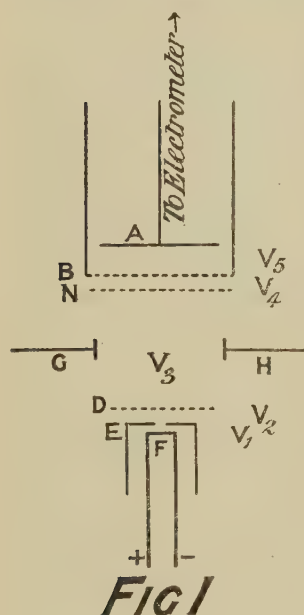
In conclusion, the writer wishes to acknowledge his indebtedness to Mr. A. Sinclair for assistance in constructing the spectrograph, and to Mr. P. H. Petrie for help in taking the spectrograms.

The Effects of Electron Collisions with Atmospheric Neon.

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Green.

(Communicated by C. T. R. Wilson, F.R.S. Received June 18, 1920.)

The present paper contains an account of an investigation of the effects of electron collisions with neon atoms by a method similar to that used with helium and with argon. The apparatus employed* is practically the same as that described in the account of the experiments with argon,† the only difference being that one of the lower gauzes (C) was removed and that two



small platinum plate electrodes were sealed into the ionisation chamber, so as to provide an electric field at right angles to the direction of the electron stream. The arrangement will be understood by reference to fig. 1, in which the lettering corresponds to that used in the earlier paper. The object of introducing the side electrodes, G and H, was to enable a second test of the production of ionisation to be made by means of a delicate galvanometer included in a subsidiary circuit.

The usual precautions for ridding the glass and the electrodes from occluded gases were taken, and in all the observations recorded in the paper a magnetic field parallel to the axis of the discharge tube was used to prevent the electron stream from spreading laterally.

The neon used was supplied to us by Dr. F. W. Aston, who had purified it by the method of repeated fractionation (over charcoal cooled in liquid air), using the apparatus he has described in the 'Philosophical Magazine,' vol. 37, p. 527 (1919). The process was repeated many times after the stage had been reached when the density of the gas was unchanged by further fractionation. The authors gladly take this opportunity of expressing their

* I wish to acknowledge my indebtedness to the Government Grant Committee of the Royal Society for the means of purchasing some of the apparatus and materials used in this research.—F. H.

† 'Roy. Soc. Proc.,' A, vol. 97, p. 1 (1920).

thanks to Dr. Aston for providing them with a sample of his purest neon. The gas was stored in a glass globe with a good stopcock, which led into a fine capillary tube, through which it passed into the apparatus, entering by way of a U-tube containing a little carbon and immersed in liquid air, this arrangement being similar to that described in the account of our experiments with helium, except for the smaller quantity of carbon employed. During the course of the research the spectrum of the neon was examined in the apparatus by means of a Hilger direct wave-length spectroscope, the luminosity being produced by the electron stream from the glowing filament, and only known neon lines were seen. The spectroscopic test is, however, not so good a guarantee of the absence of impurities as the density observations of Dr. Aston.

Preliminary Experiments.

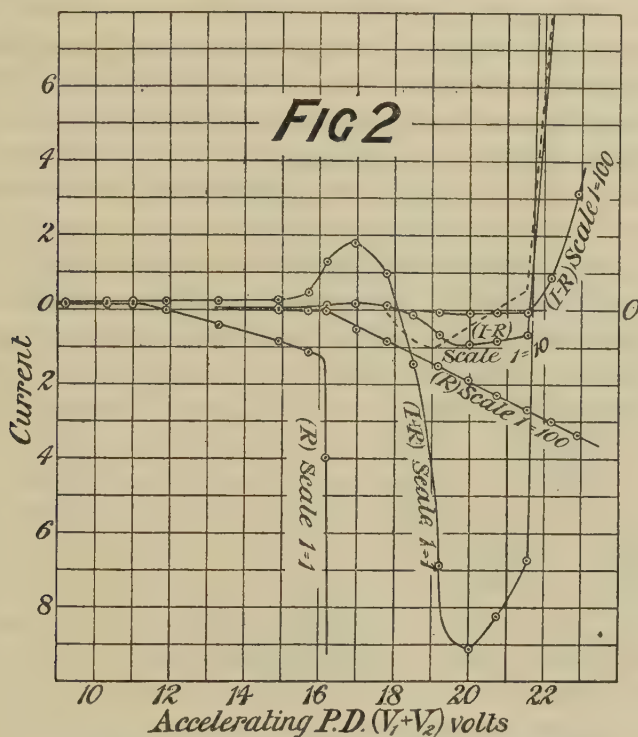
For the general investigation of the effects of electron collisions with neon atoms, and for the determination of the approximate values of the critical velocities for electrons in this gas, the various electric fields were so arranged that when a critical velocity was reached the electrons should be able to make collisions over a considerable distance before their velocity was reduced below the critical value. This condition was secured by having the gauze D and N at the same potential, and by turning back the electrons in the space between the gauzes B and N. The immediate production, throughout the whole of the ionisation space, of radiation or ionisation, as the case might be, when a critical velocity is reached, is thus made possible, and the chances of detecting the radiation or ionisation as soon as it is produced are increased.

In all the preliminary experiments the electrons were accelerated up to the gauze D by the fields V_1 and V_2 , of which V_1 had the constant value 7 volts, while the variation of the speed of the electrons entering the space between the gauzes D and N was affected by the gradual increase of the potential difference applied between E and D. Of the two side electrodes, G and H, one, G, was maintained at the same potential as the gauzes D and N, while the other side electrode, H, was either maintained at a potential of -3 volts with respect to G, or was kept at the same potential as G, according as it seemed desirable or not to restrict the number of positive ions reaching the collecting electrode. The electrons in the stream from the filament were prevented from reaching the plate A by the opposing potential difference applied between B and N, which was sufficiently great to turn them back to the gauze N. The electrometer should therefore give no indication of a current until the velocity of the electrons is such that their collisions with gas atoms give rise to either radiation or ionisation. When radiation is

produced in the gas, the resulting photo-electric current will be positive or negative according as the plate A is negative or positive with respect to the gauze B. When ionisation is produced in the gas, its detection depends upon the diffusion of the positive ions from the space between the gauzes D and N into the space between the gauzes N and B, where they are accelerated towards the plate A by the potential difference, V_4 , which retards the electron stream. If the gauze B is at a positive potential with respect to the plate A, positive ions will be further accelerated towards the collecting electrode. In this case the photo-electric effect of the radiation acting on the plate A gives a positive current, so that both radiation and ionisation tend to give a current in the same direction, and for this reason curves taken with this arrangement of fields will be referred to as (I+R) curves. If the gauze B is at a negative potential with respect to the plate A, radiation will give a negative current, while the collection of positive ions produced by ionisation will depend upon whether the opposing potential difference, V_5 , is sufficient to turn them back or not. Curves in which the positive ions are able to reach the collecting electrode in spite of an opposing field, V_5 , will be referred to as (I-R) curves, since in this case the radiation current will be opposite in direction to the ionisation current. In curves of this type a positive or a negative current will be obtained according as the effect of ionisation or of radiation predominates. Series of observations in which the positive ions are prevented from reaching the collecting electrode by the opposing field, V_5 , will be referred to as R curves, since in these circumstances the electrometer measures the radiation current alone.

Typical examples of (I-R) curves and R curves are given in fig. 2. These two series of observations were taken simultaneously, corresponding points on the two curves being taken consecutively. In this way the two series were obtained under identical conditions. The average pressure of neon in the apparatus during these experiments was 0.025 mm. The R curve, considered alone, shows that a negative current indicating radiation is first produced when the applied accelerating potential difference is about 11 volts, and that a sudden increase in the amount of radiation produced takes place when the applied potential difference is increased to about 16 volts. In the (I-R) curve, the effect of the radiation, which the R curve indicates as being produced when the accelerating potential difference has a value of about 11 volts, is obscured by the secondary effects of the bombardment of the gauze N by the electron stream. This curve, however, shows that a positive current, increasing with $(V_1 + V_2)$, begins when this potential difference has a value of about 15 volts. The curve begins to turn down when $(V_1 + V_2)$ is between 16 volts and 17 volts, the positive current decreasing, and an

increasing negative current being obtained. This negative current continues to increase until the accelerating potential difference reaches a value between 19 volts and 20 volts, after which it gradually decreases. Another bend in



The broken $(I-R)$ curve, scale 1-10, represents observations with decreasing values of (V_1+V_2) .

the curve is obtained when the applied accelerating potential difference is increased to about 21.5 volts, after which the curve slopes up at a greatly increased rate, indicating a rapidly increasing positive current. Considering the $(I-R)$ curves and the R curves together, it will be observed that, at the three stages at which the $(I-R)$ curves turn towards the positive direction, namely, about 15 volts, between 19 volts and 20 volts, and between 21 volts and 22 volts, the R curve shows no change of slope. The three stages mentioned may therefore be taken as giving indications of the increased production of ionisation rather than a reduction in the amount of radiation produced. As a result of the preliminary experiments, of which these curves are typical, it was decided to investigate the following points in greater detail:—

1. The production of radiation at an applied potential difference of about 11 volts.

2. The increased production of radiation at an applied potential difference of between 16 volts and 17 volts.

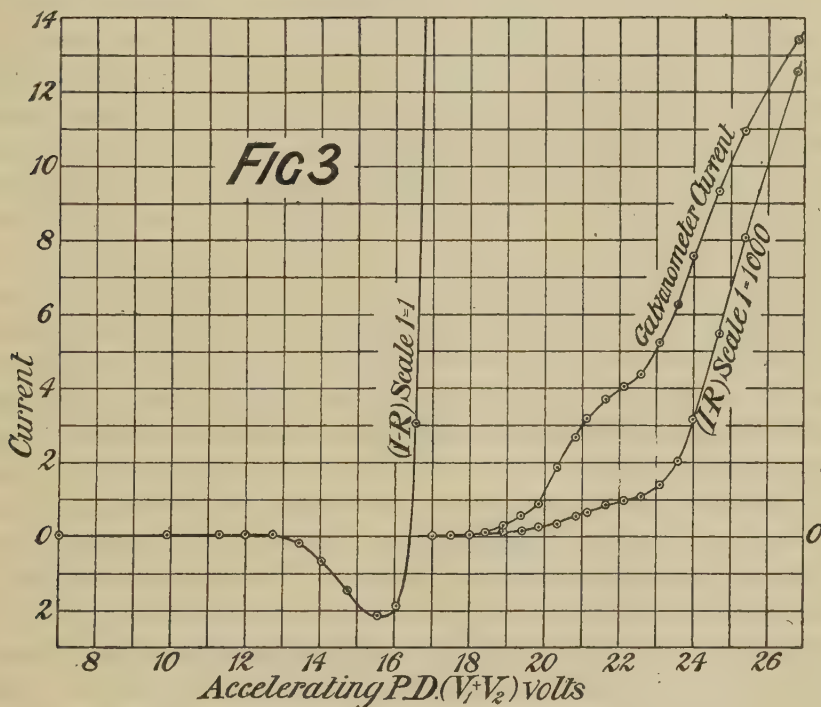
3. The production of ionisation at an applied potential difference of about 15 volts.

4. The increased production of ionisation at an applied potential difference of between 19 volts and 20 volts.

5. The further increased production of ionisation at an applied potential difference of between 21 volts and 22 volts.

Before passing on to the more detailed investigation, it must be mentioned, in connection with the preliminary experiments, that, in some cases, another type of (I—R) curve was obtained. While, in every case investigated, the R curve gave an indication of the increased production of radiation at an applied potential difference of between 16 volts and 17 volts, some instances of (I—R) curves were obtained where no indication of this second type of radiation was shown, but where the positive current increased steadily from an applied potential difference of 15 volts until one of the higher ionisation velocities was reached. In these cases, it is clear that the ionisation of the type produced at an applied potential difference of 15 volts must have been considerably in excess of the radiation of the type produced at an applied potential difference of between 16 volts and 17 volts. The occurrence of these two types of (I—R) curves suggests that the ionisation and radiation concerned are to be attributed to different kinds of atomic systems. Curves showing two radiation velocities were usually obtained when neon at a low pressure was streaming through the apparatus immediately after it had been highly evacuated and the carbon purifying tube had been heated to drive out the occluded gas, while, in general, curves of the second type were obtained with gas that had been present in the apparatus a longer time. (I—R) curves of the first type could sometimes be obtained by the use of a very small electron stream under conditions when the employment of a larger electron stream gave (I—R) curves of the second type. An illustration of an (I—R) curve of this type is given on two scales in fig. 3. During the series of observations represented in this figure, the gauzes N and D were at the same potential, but the side electrode, G, was at a negative potential of 5.6 volts with respect to the negative end of the filament. The other side electrode, H, was at a negative potential of 17 volts with respect to G, and the circuit between these two electrodes included a galvanometer. As both the side electrodes were negatively charged with respect to the gauze D, the maximum velocity the electrons acquire is that with which they pass through this gauze. With the arrangement of electric fields indicated, the current measured by the galvanometer was that due to ionisation alone

since the side electrodes were too small for the radiation to cause a photo-electric current measurable on the galvanometer. By comparing the electrometer and galvanometer current curves in fig. 3, it will be observed that, when ionisation was first detected by the electrometer, the amount of ionisation produced was too small to give an indication on the galvanometer. Though the beginning of ionisation was not detected by the galvanometer, this instrument gave clear indications of the increased production of ionisation at an applied potential difference of between 19.5 volts and 20 volts, and again between 22 volts and 23 volts.



In some instances, the investigation was complicated by the sudden occurrence of a large increase in current, which was detected simultaneously in both R and (I-R) series of observations. The increase of current observed in the (I-R) series was an increase of positive, or ionisation current. This is similar to an effect recorded in the account of our experiments with argon. The increase was most marked in cases where a large electron emission was used, and when the gauzes N and D were at the same potential. It did not always occur for the same value of the applied accelerating potential difference, but in no instance was it obtained for a value of this potential difference less than about 16 volts. In the case of

argon, this phenomenon was attributed to an enormously increased effective emission resulting from the neutralisation of the space charge effect by positive ions travelling down to the filament. In the case of neon, it was found that the effect was not obtained when the fields were so arranged that positive ions could not readily pass down to the filament, a fact which supports the explanation suggested. Attempts to detect directly an increase in the effective emission from the filament were, however, not successful.

The Exact Determination of the Critical Velocities.

The critical points found in the experiments described in the earlier section of the paper have been referred to the values of the applied accelerating potential difference at which the effects are indicated in the curves. In attempting to determine accurately the value of the minimum electron velocity at which any given effect could first be obtained, it is necessary to make a correction to the observed accelerating potential difference to allow for the velocity of emission from the filament of the electrons which produce the effect. In previous communications the authors have based their determination of the magnitude of the correction to be applied in any given instance upon the assumption that the number of electrons present in the stream from the filament, having the velocity of the swiftest that could be detected, was sufficient to give a detectable amount of radiation or of ionisation when a critical point was reached. The correction was found by determining the value of the retarding potential difference which had to be applied in order to prevent electrons from the filament, accelerated by a given potential difference, from reaching the collecting electrode in sufficient quantity to be detected by the electrometer, and by taking the difference between the applied retarding and accelerating potential differences, when this stage had been reached, as the correction. It was realised that the values of critical velocities deduced in this way might be rather higher than the true values, but the results obtained for certain critical points by methods which yielded values free from the necessity for correction tended to confirm the values which were dependent upon the application of a correction, and showed that in these cases the error involved in taking as the value of the critical velocity that of the swiftest electrons present when a critical stage was reached, could not be serious.

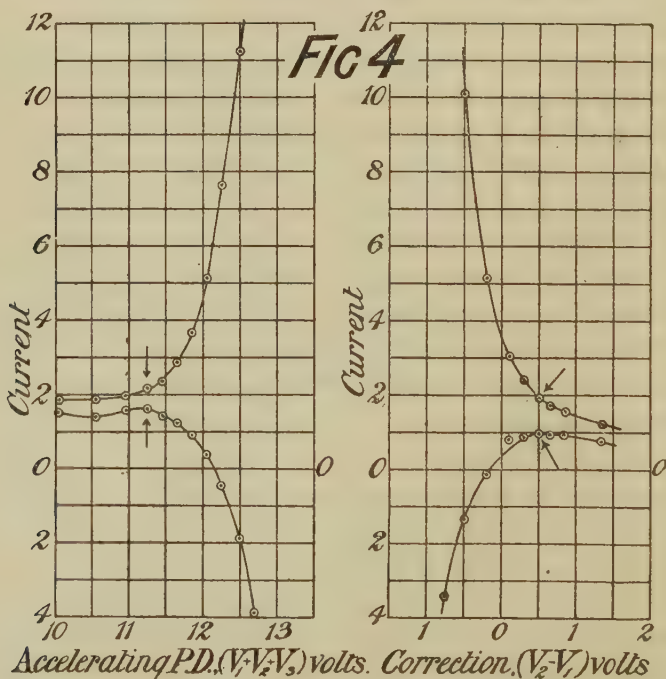
In the present investigation considerable ranges of pressures and intensities of electron stream were employed in different series of observations, and it was found that the values of the correction varied over a wider range than the corresponding applied potential differences at which the effects were observed in the curves. This was particularly noticeable in the case of the first

radiation point. It was, therefore, clear that with the form of apparatus and the arrangement of fields employed in this investigation an error was involved in taking the correction from the swiftest electrons present. The correction to be applied to any given critical stage was therefore determined by ascertaining the highest value of the retarding potential difference which could be applied to allow electrons from the filament, accelerated by a given potential difference, to get through against the retarding field in sufficient quantity for them to produce a detectable amount of radiation or of ionisation under conditions as nearly as possible the same as those employed in the actual experiment. This was done by giving the field V_1 , between the filament and E, a constant value—about 5.8 volts in most of these experiments—and by applying between E and D a retarding potential difference by the variation of which the number of electrons getting through into the space between D and N could be controlled. Between D and N a constant accelerating potential difference was applied, the value of which was fixed a little above the value found for the critical velocity for which the correction was under investigation, this velocity having been deduced in the manner of our earlier researches. This ensured that *all* the electrons passing into the space between the gauzes D and N against the opposing potential difference V_2 would be able to acquire the critical velocity in question. The two side electrodes were maintained at the same potential as the gauze D. Between the gauzes N and B a constant retarding potential difference was applied, sufficient to prevent any of the original electrons reaching the collecting electrode. The final potential difference between the gauze B and the plate A was fixed according as it was desired to detect the effect in question in an (I+R), an (I-R), or an R curve. The retarding potential difference V_2 , which controlled the number of electrons used, was then varied until the electrometer first indicated a radiation or an ionisation current, as the case might be. When this stage is reached, it is clear that the number of electrons passing through into the space between D and N is the minimum number required to give a detectable effect (of the type under investigation) with the special arrangement of fields used. The (I-R) or R curve from which a value of a critical point is to be deduced must be taken with as nearly as possible the same arrangement of fields as that employed in estimating the correction, and in this case it is clear that the correction to be added to the observed value must be the difference between the potential differences V_2 and V_1 , when V_2 is adjusted to give the minimum number of electrons necessary for the effect to give a detectable current. It was found that the corrected values of critical velocities, determined in this way, showed very little, if any, variation when deduced from series of observations taken

with intensities of electron stream and gas pressures which varied over a considerable range from series to series.

The Minimum Radiation Velocity.

In order to be able to apply the correction found in the manner described above to obtain a value of a critical velocity from a series of observations of the variation of current with increasing accelerating potential difference, it was necessary that the series of observations should be taken with the variable part of the accelerating potential difference applied between the gauzes D and N, the fields V_1 and V_2 being constant accelerating fields. Therefore, in all the curves from which accurate values of critical velocities have been deduced, it was not possible to maintain the gauzes D and N at the same potential and to allow the radiation or ionisation to be produced throughout the whole space at once, as in the preliminary experiments. The series from which accurate values of the first radiation velocity were deduced were of two types. In one type the radiation current was examined alone in an R series, the correction being also deduced from observations with the field V_5 arranged for an R curve. In the second type (I-R) and (I+R) series of observations were taken simultaneously, corresponding points on the two curves being taken consecutively. The point of divergence of these two



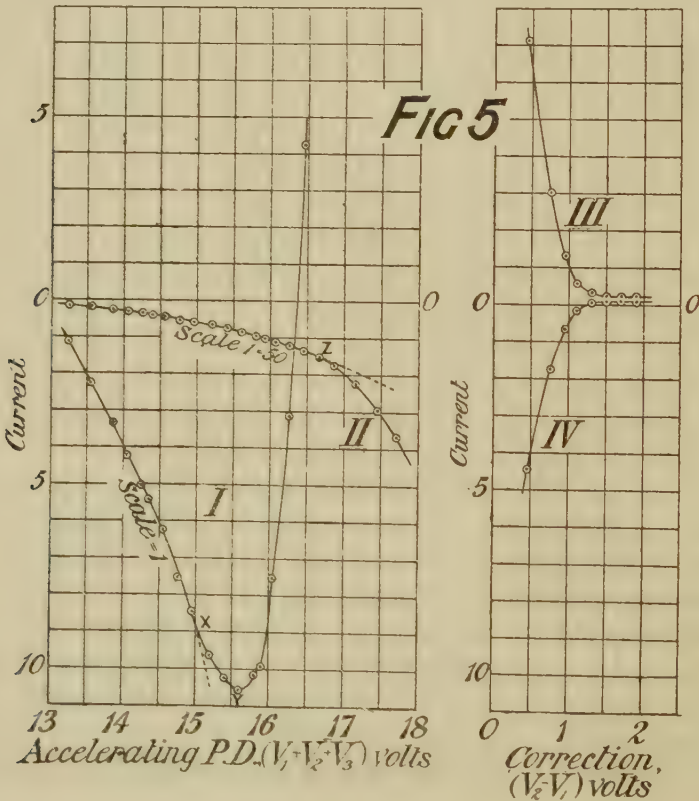
curves was taken as indicating the beginning of radiation. In obtaining the correction for this type of series ($I+R$) and ($I-R$) sets of observations were also taken simultaneously for different values of V_2 , and the value of V_2 at which these began to diverge was used for deducing the correction. The corrected values of the minimum radiation velocity, obtained by the two methods, varied between 11.75 volts and 11.95 volts. The mean of all the results—11.8 volts—was therefore taken as the value of the first radiation velocity. An example of ($I-R$) and ($I+R$) series, with the corresponding curves for the correction, from which a value was deduced, is given in fig. 4. These curves were taken with neon at an average pressure of 0.133 mm. in the apparatus.

The Minimum Ionisation Velocity.

The type of curve from which it was found that values of the minimum ionisation potential difference could be obtained most satisfactorily was the ($I-R$) curve. This involved the detection of the beginning of ionisation in the presence of the negative current due to radiation of the first type. The ionisation current always increased much more rapidly with increasing electron velocity than the current due to the first radiation, so that it was possible to adjust the temperature of the filament so that the radiation current should be quite small and almost negligible without also reducing the ionisation current to the stage when it would be difficult to detect its beginning. In cases where a very small electron stream was employed and the current due to the first radiation was negligible, the detection of the beginning of ionisation depended upon the first indication of an increasing positive current. Where the negative current due to radiation was not negligible, the detection of the beginning of ionisation depended upon the determination of the first point at which the rate of increase of the negative current showed signs of diminishing. Series of observations were taken at average pressures, ranging from 0.006 mm. to 0.310 mm., and for several different values of the intensity of the electron stream.

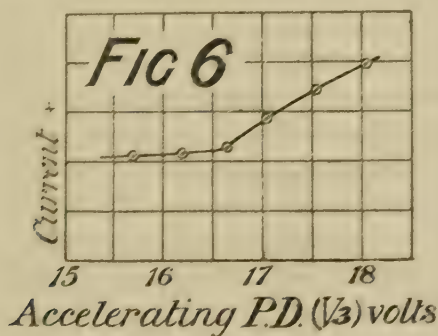
In determining the correction (to be applied in order to obtain the minimum ionisation velocity), the arrangement of the fields V_4 and V_5 had to be that required for an ($I-R$) series. It was anticipated that there might be some difficulty in estimating this correction, owing to the possibility that, when V_3 had been adjusted to a value just sufficiently great to ensure that all the electrons should be able to acquire the velocity necessary for the first ionisation, some of the electrons getting into the space between the gauzes D and N might produce radiation of the first type instead of ionisation. Collisions resulting in the production of radiation from the gas

would tend to give a negative current, and, if this negative current were large enough for the electrometer to give an indication, the value of V_2 , for which an increasing *positive* current was first obtained, would not give the true correction. It was found, however, in practice, that, for a given value of V_1 , the limiting value of V_2 , for which a detectable amount of ionisation was produced, was considerably higher than the value of V_2 , for which a detectable amount of the first radiation was produced with a suitably adjusted V_3 . In other words, more electrons having a velocity slightly in excess of the minimum radiation value, are required to give a detectable radiation current, than are required to give an indication of ionisation when their velocity is slightly in excess of the minimum ionisation velocity. Thus the anticipated difficulty does not arise, since, at the stage when ionisation is detected, the number of electrons concerned is insufficient to give a measurable current due to radiation of the first type. The corrected values of the minimum ionisation velocity, deduced from curves taken under very different conditions of pressure and intensity of electron stream, are in good agreement, the mean corrected value being 16.7 volts. An example of



a curve from which a value has been deduced, together with the corresponding correction curve, is given in fig. 5 (curves I and III). The series of observations represented in this curve were taken at an average pressure of 0.121 mm. From the curve, it is clear that, though the negative current does not actually cease to increase until the point marked Y is reached, the downward slope of the negative current curve begins to get less at the point marked X, so that the latter point is taken as giving the first indication of the beginning of ionisation. The applied accelerating potential difference at the point marked X is 15.05 volts, and, from the correction curve III, it is clear that the correction to be added to this is +1.5 volts, so that the value of the minimum ionisation velocity deduced from this figure is 16.55 volts, which differs very little from the mean of all the accurately determined values.

The curve given in fig. 6 affords interesting confirmation of the value we have deduced for the minimum ionisation velocity by applying the correction obtained in the manner described. In taking the series of observations illustrated in fig. 6, the fields were arranged for the determination of the limiting value of V_2 for which a detectable ionisation current was first produced when V_2 had such a value that all the electrons getting into the space between the gauzes D and N would have an opportunity of acquiring the minimum ionisation velocity. The limiting value of the retarding field, V_2 , was ascertained, and V_2 was then reduced 0.2 volt below this limiting



value, so that there could be no doubt that a sufficient number of electrons to give a clear indication of ionisation were being permitted to enter the space between D and N. The accelerating potential difference, V_3 , was then gradually increased from a value clearly too low to give the electrons the necessary velocity for the production of ionisation, up to about 18 volts. Under these conditions, the value of V_2 , at which an increasing positive current begins, should give the value of the minimum ionisation velocity

independent of correction, except for the 0.2 volt acquired from the fields V_1 and V_2 . It will be observed from fig. 6 that the rise in the curve begins when V_3 is 16.6 volts, which gives 16.8 volts as the minimum ionisation velocity, a value in good agreement with the mean value given above.

The Second Radiation Velocity.

The preliminary experiments described in an earlier section of the paper suggested the production of a second type of radiation at an applied potential difference of between 16 volts and 17 volts. This is indicated in both the (I—R) curve and the R curve given in fig. 2. It will be noticed that the indication of this second radiation in the curves falls near the mean value we have given for the minimum ionisation velocity, namely, 16.7 volts. It has also been pointed out that the correction which was found for the first ionisation potential difference is greater than the correction which had to be added to the observed value of the applied potential difference to give the first radiation velocity. The difference between these two corrections in some cases amounted to as much as 0.8 volt. If the correction for the second radiation velocity is the same as that found for the first radiation velocity, the first ionisation point and the second radiation point are actually even closer together than they appear to be from the curves. It therefore seemed desirable to take special series of observations, to investigate whether the first ionisation and the second radiation occur simultaneously.

The type of curve from which most of the accurate values of the second radiation velocity have been deduced was that given by R series of observations. Curves of this type were taken in preference to (I—R) series for the reason given earlier, namely, that (I—R) series did not always give an indication of the second type of radiation. The detection of the beginning of the second radiation therefore depends upon the determination of the point in the R curve, at which the slope increases abruptly. R series of observations for the determination of the second radiation velocity, were taken at average pressures ranging from 0.486 mm. to 0.009 mm., and for different intensities of the electron stream. The values deduced from these curves, and from some (I—R) curves, differed very little from the mean of all the corrected values, namely, 17.8 volts. The special test for the simultaneous occurrence of the first ionisation and the second radiation consisted in taking an (I—R) series of observations for the determination of the first ionisation velocity simultaneously with an R series for the estimation of the second radiation velocity, corresponding points on the two curves being taken consecutively. In the same way, corresponding points on an R correc-

tion curve and on an (I—R) correction curve were taken consecutively. It was thus possible to ascertain with certainty whether the two effects were produced at the same electron velocity or not. An example of such a pair of curves is given in fig. 5. Curves I and III of this figure have already been considered. The curves II and IV are respectively the radiation curve, and the corresponding R correction curve. I and II show clearly that the interval between the applied potential differences at which the first ionisation and the second radiation are first indicated is at least 1 volt. The correction curves III and IV show that radiation and ionisation begin to be detectable for the same value of V_2 , namely, when $(V_2 - V_1) = 1.5$ volts, thus giving a positive correction of 1.5 volts for both the radiation and the ionisation. The detection of a radiation current in the R correction curve when $(V_2 - V_1) = 1.5$ volts does not, however, constitute a proof that this is the correction which has to be added to the applied potential difference at which the bend in the R curve occurs, in order to obtain the second radiation velocity, since it is possible that the observed current in curve IV is due to radiation of the first type.

It has already been pointed out that, when V_3 is only slightly greater than the first radiation velocity, many more electrons are required to give a detectable radiation current than are required to give a detectable ionisation current when V_3 is slightly greater than the first ionisation velocity, *i.e.* $(V_2 - V_1)$ must be much smaller in the case of the first radiation than in the case of the first ionisation, for which it is here shown to be 1.5 volts. The radiation current produced by a given number of electrons will, however, increase as the velocity of the electrons increases, so that it is possible that, though with $(V_2 - V_1)$ equal to 1.5 volts, the 11.8 volt radiation current is too small to be detected when V_3 is about 12 volts, it may be measurable when V_3 is about 18 volts. This point was tested, by determining for a given pressure and intensity of electron stream, the limiting value of the retarding potential difference, V_2 , for which a detectable current was obtained, for different values of V_3 , with the electric fields arranged as for an R series. In the particular case tested, it was found that, as V_3 was increased, the limiting value of V_2 at first increased slightly, but soon reached a constant value. This constant value gave a correction of +1.0 volt. When, however, V_3 had been increased to such a value that the second radiation could be occurring, it was found that the limiting value of V_2 changed abruptly to a value which gave a correction of +1.5 volts. The correction deduced from the limiting value of V_2 then remained the same as V_3 was further increased. The results of these experiments provide sufficient justification for attributing the negative current, beginning when

($V_2 - V_1$) was equal to 1.5 volts, to the second type of radiation. The curves of fig. 5 may therefore be taken as showing conclusively that the first ionisation and the second radiation do not occur simultaneously.

In deducing a value of the second radiation velocity from an R curve, such as curve II (fig. 5), the question arises as to whether the amount of the second radiation produced by the number of electrons concerned in first producing a measurable effect in the correction curve IV, would be detectable in the presence of a negative current due to the first type of radiation, when this current is of considerable magnitude. In estimating (from the curves given in fig. 5) the interval between the first ionisation velocity and the second radiation velocity, it seems probable that the points Y and Z are corresponding points, rather than the points X and Z, for it seems improbable that an increase of radiation which would correspond to the ionisation current between the points X and Y in the (I-R) curve would be sufficient to show in the R curve. The interval between the points Y and Z in these curves is 16.75 volts - 15.6 volts = 1.15 volts, which gives, as the corrected value of the second radiation point ($16.55 + 1.15 =$), 17.7 volts, a value in good agreement with the mean value (17.8 volts) already given. The value 17.8 volts, found in the manner indicated, was confirmed in the same way as the value found for the first ionisation velocity, by taking an (I-R) series of observations with the fields arranged as for the determination of a correction, and with V_2 (the retarding potential difference) adjusted to 0.2 volt less than the limiting value. During these observations, neon was streaming through the apparatus at a low pressure, and it was found that the second type of radiation was able to overcome the first type of ionisation, and to turn the curve down. The accelerating potential difference, V_3 , at which the first indication of the second type of radiation was obtained, gave 17.8 volts for the second radiation velocity, thus confirming the value already obtained.

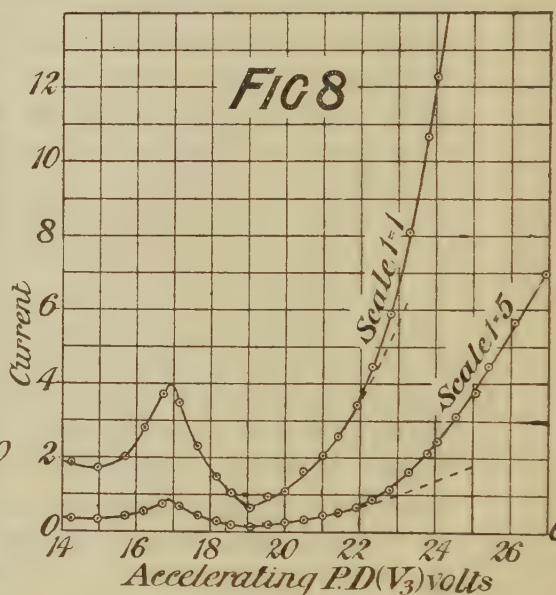
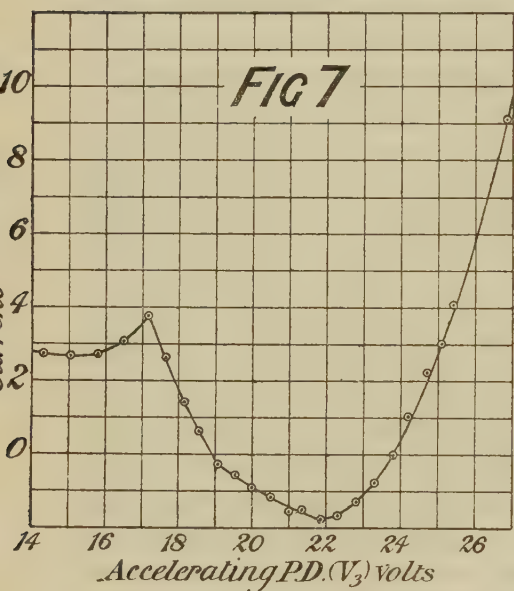
The Second and Third Ionisation Velocities.

In addition to the ionisation and radiation velocities already investigated in detail, the preliminary experiments indicated the increased production of ionisation at an applied potential difference of about 19 volts, and again at about 22 volts. Of these, the increased ionisation at about 22 volts was much the more marked effect of the two, and in some instances the curves gave no sign of the increase at about 19 volts. Owing to the difficulty of determining just where the increase of current begins when this increase has to be detected in the presence of an already considerable current of the same sign, it was decided that the most reliable values for the second and third ionisa-

tion velocities would be obtained if the indication of an increase of ionisation were sought for in the presence of a negative current. It was found that curves of the required type were best obtained by using a smaller electron emission than that employed hitherto, and by having neon streaming slowly through the apparatus, the purifying carbon tube having been strongly heated and pumped immediately before cooling in liquid air and commencing the series of observations. In order to obtain the desired type of curve and the necessary correction under as nearly the same conditions as possible, the (I—R) curves were taken with the potential difference V_2 retarding, instead of accelerating, the electron stream. In the first place, the limiting value of V_2 to give a detectable ionisation current with an (I—R) arrangement of fields was ascertained for different values of the accelerating potential difference V_3 , ranging from about 17 volts to 25 volts. No appreciable change in the limiting value of V_2 was found when different values of V_3 were employed, so that the correction for the higher ionisation points cannot be greater than the correction for the first ionisation point. When neon was streaming through at a low pressure it was found that, though the limiting value of V_2 (the retarding potential difference) changed very little as V_3 was given the various different values, yet in some cases the current measured by the electrometer was positive, while in others it was negative. For instance, in one such investigation made for the following three values of V_3 , 17.15 volts, 20.0 volts, and 25.5 volts, the limiting value of V_2 was in each case found to be 6.6 volts. With V_3 equal to 17.15 volts, starting with $V_2 = 6.6$ volts and gradually reducing it, an increasing positive current was first obtained. This positive current began to decrease with further reduction of V_2 below 5.8 volts, indicating that the difference between 5.8 volts and the limiting value 6.6 volts, *i.e.*, 0.8 volts, added on to 17.15 volts, was sufficient to enable the electrons to give rise to the second type of radiation. When V_3 had the value 20.0 volts, a gradually increasing *negative* current was obtained as V_2 was reduced below 6.6 volts, while in the third case, where V_3 was 25.5 volts, an increasing *positive* current resulted from the same variation in V_2 . Since the radiation produced at 17.8 volts is able to overcome the 16.7 volt ionisation, the detection of a positive current for this last value of V_3 , even when V_2 had the limiting value, shows that in this case the correction corresponding to this limiting value applies to one of the higher ionisation velocities. Thus, the correction found for the first ionisation velocity can also be used to obtain the higher ionisation points.

In making a determination of one of these higher ionisation velocities, the limiting value of V_2 for which an ionisation current could be detected when V_3 was about 24 volts was first ascertained, and then V_2 was reduced below

this limiting value by 1.0 volt and an (I-R) curve taken by gradually increasing V_3 , starting from 14 volts. The reduction of V_2 below the limiting value which lets through the minimum number of electrons necessary to give a detectable current, serves to increase the velocity of this minimum number, and so the correction to be added to the values of V_3 at which indications of increased ionisation were shown in the curve obtained, is thus 1.0 volt. The small electron emission, still further limited by the retarding field V_2 , serves to keep the currents measured by the electrometer small, and also tends to prevent the complication introduced by the simultaneous large increase of radiation and of ionisation sometimes observed, which was attributed to neutralisation of the space charge near the filament. Two curves are given below in figs. 7 and 8 which are typical of the results obtained in experiments of this kind, and from which values of the second and third ionisation



velocities can be deduced. During each of these series of observations, the side electrodes G and H were maintained at the same potential as the gauze D, and V_2 was in each case 1.0 volt below the limiting value, so that the correction to be applied to values read from the curves is 1.0 volt. The average pressure during the series of observations represented in fig. 7 was 0.063 mm. This curve shows the first ionisation beginning when V_3 is equal to about 15.7 volts and increasing as V_3 is increased up to about 17 volts, after which it decreases, owing to the production of the second type of radiation. In this curve, when V_3 is increased to 19 volts, the downward slope

of the curve changes and indicates the production of the second type of ionisation. A further change in the curve occurs when V_3 is equal to 21·8 volts, for after this point the negative current rapidly decreases as V_3 is increased and finally gives place to an increasing positive current. In fig. 8 the occurrence of ionisation at 19 volts causes an abrupt upward bend in the curve at this point, and the increase of ionisation at 21·8 volts is shown by the increased slope of the curve after this value is passed. The mean corrected values of the second and third ionisation velocities as deduced from these curves are 20·0 volts and 22·8 volts respectively. The values are in good agreement with the values obtained from a large number of curves, representing observations taken over a range of pressures extending from an average pressure of 0·007 mm. to an average pressure of 0·310 mm. The main differences in the conditions under which the curves in figs. 7 and 8 were taken, were that, in the case of fig. 8, the average pressure was a little higher than in fig. 7 and a rather stronger electron stream was used.

The mean values obtained for the different critical velocities by the detailed experiments described in this section are as follows :—

	Volts.
Minimum radiation velocity	11·8
Second radiation velocity	17·8
Minimum ionisation velocity	16·7
Second ionisation velocity	20·0
Third ionisation velocity	22·8

Previous investigations of the effects of electron collisions with neon have been made by Franck and Hertz,* and by Rentschler.† Franck and Hertz obtained evidence which they interpreted as indicating the occurrence of ionisation at 16 volts, but, as the method they employed did not make it possible to distinguish between ionisation and radiation, their experiments can only be taken as indicating the existence of a critical velocity at this point. Rentschler concluded from his experiments, by the method used by Tate and Foote‡ with metallic vapours, that neon did not show a resonance (or radiation) velocity, and that its ionisation velocity was 19·5 volts. In the course of the present research, the authors carried out several experiments based on the method of Tate and Foote, but found that the resulting curves did not indicate some of the critical velocities which the experiments described in this paper have shown to exist. A discussion of the reasons for

* J. Franck and G. Hertz, 'Deutsch. Phys. Ges. Verh.,' vol. 15, p. 34 (1913).

† H. C. Rentschler, 'Phys. Rev.,' vol. 14, p. 503 (1919).

‡ J. T. Tate and P. D. Foote, 'Phil. Mag.,' vol. 36, p. 64 (1918).

the failure of this method, when used for gases in which the critical velocities are high, has been given elsewhere.*

Discussion of Results and Conclusion.

The fact that in neon it has been found that there are two critical electron velocities associated with the production of radiation from the gas, and three critical velocities associated with the production of ionisation, all these values being less than 25 volts, suggests that neon differs more in constitution from helium and argon than would be expected from its position in the Table of Elements. It might be suggested that the second radiation velocity, 17.8 volts, and one of the higher ionisation velocities, are analogous to the critical velocities found in helium corresponding to the displacement and to the complete removal, respectively, of the second electron from the atom. In this case, the values referred to above for neon would be either—

(a) The electron velocity required to produce further radiation or ionisation respectively from already ionised atoms; or

(b) The electron velocity necessary for the production simultaneously of the 16.7 volt ionisation, and additional radiation or ionisation respectively.

Experimental evidence, which makes both of these possibilities seem unlikely, is provided by several series of observations, taken when neon was first entering the apparatus. These series of observations gave curves in which no indication of the critical velocities at 11.8 volts and 16.7 volts was obtained, while those at 17.8 volts and 22.8 volts were plainly shown. It is therefore clear that the effects produced at these higher velocities cannot be dependent upon the presence of positive ions of the kind resulting from the 16.7 volt ionisation. The same experiments constitute an objection to the view that 17.8 volts and 22.8 volts, respectively, correspond to the energies necessary for the production simultaneously of the 16.7 volt ionisation and additional radiation or ionisation, for it is very improbable that the double ionisation of the atom would give a considerable current, when the simple ionisation did not give a measurable effect. On theoretical grounds, the alternative (b) is extremely unlikely, since the quantities of energy concerned are so small compared with the quantities required to produce similar effects in helium. Moreover, if (b) were the true explanation, the electron velocities required for the displacement and complete removal, respectively, of a second electron from an already ionised atom would be $(17.8 - 16.7 =) 1.1$ volts and $(22.8 - 16.7 =) 6.1$ volts, which are lower than the corresponding electron velocities for the normal atom. It does not, therefore, seem possible to reconcile the observed effects with the

* F. Horton and A. C. Davies, 'Phys. Rev.', vol. 15, p. 498 (1920).

view that, at one of the higher critical ionisation velocities, doubly charged atoms are produced.

The accepted view of the connection between the quantities of energy required for the production of radiation and of ionisation is that they correspond to the first and to the limiting frequency, respectively, of some particular spectral series of the element concerned. On this view, it would be expected that, with every ionisation velocity, there would be associated a definite radiation velocity. In our experiments, evidence of three ionisation velocities and of only two radiation velocities was obtained. It is unlikely that the absence of any indication of a third radiation velocity can be explained by supposing that a third radiation is produced, but is of too small a frequency to give a photo-electric effect, since the three ionisation velocities correspond to frequencies well within the Lyman region of the spectrum. It is possible, however, that two radiation velocities occur so close together that they do not give separate indications in the curves, in which case one of them would escape detection. Whatever view is taken of the origin of the effects occurring at different critical velocities, it seems necessary that a definite radiation velocity should be associated with each ionisation velocity, and it therefore seems probable that, unless one radiation velocity is escaping detection, the ionisation observed at one of the three critical velocities is a spurious effect. The electron velocity, 20.0 volts, at which the second ionisation was detected, is in fair agreement with the value we found for the minimum radiation velocity for electrons in helium (20.4 volts), if allowance is made for the difference in the methods employed in determining the correction in the two cases. If helium were present as an impurity in the neon used, radiation would be produced in the gas when the electron velocity reached 20.4 volts, and this radiation would be of sufficiently high frequency to cause the ionisation of the system to which the ionisation velocity of 16.7 volts is attributable. The radiation produced at 20.4 volts might therefore show, as an increase of ionisation current rather than as an increase of radiation current, and in this case no further change in the ionisation current would be expected when the ionisation velocity of helium (25.6 volts) was reached, since the direct ionisation of this gas by collisions might not result in the production of more positive ions than the indirect ionisation of the neon by the 20.4 volt helium radiation. The presence of helium as an impurity would thus provide a possible explanation for the additional ionisation velocity observed, but, against the adoption of this explanation, must be placed the fact that the neon used had been subjected to a lengthy series of fractionations to purify it from helium, and no trace of this gas could be detected by other means. The explanation.

given would, of course, hold equally well if a small proportion of any element having a radiation velocity of about 20 volts were present.

With regard to the two radiation velocities and the ionisation velocities at 16·7 volts and 22·8 volts, experimental evidence makes it appear probable that the radiation velocity 11·8 volts is associated with the ionisation velocity 16·7 volts, and that the radiation velocity 17·8 volts is associated with the ionisation velocity 22·8 volts, for in certain series of observations, already referred to, the 11·8 volt radiation and the 16·7 volt ionisation could not be detected, while the other critical velocities were strongly indicated. On theoretical grounds it is difficult to imagine any other association of these radiation and ionisation velocities, for the ionisation velocity must be higher than the radiation velocity associated with it.

We may, therefore, assume that if neon consists of two or more constituents having different radiation and ionisation velocities, the critical velocities 11·8 volts and 16·7 volts are to be attributed to one constituent, and the critical velocities 17·8 volts and 22·8 volts to another. The positive ray experiments of Sir J. J. Thomson* and the more recent experiments of Dr. Aston† on the mass spectra of the elements have shown that neon contains two constituents of atomic weights 20·00 and 22·00, and possibly a very small proportion of a third constituent, of atomic weight 21·0. A consideration of the arrangement of the elements according to the Periodic Law shows that the existence of *different* elements with these atomic weights is not in accordance with the principle of atomic numbers, and the constituents of neon are considered by Aston to be isotopes. In this case they have the same nuclear charge and the same number of surrounding electrons, which might be expected to be distributed in the same way about the nucleus in each case. On this view it is difficult to see how the presence of two or more isotopes can account for the existence of two radiation velocities and three ionisation velocities. If neon consists of a mixture of two or three different elements of the same group, one having an ionisation potential difference of 16·7 volts and another having an ionisation potential difference of 22·8 volts, the spectrum of the gas should show some lines when excited by electrons having a velocity of 22·8 volts or more, which would be absent when the velocity of the exciting electrons was less than this. Attempts were made to detect differences in the visible spectrum when electron velocities above and below this limit were used, but the experiments showed that, in order to obtain conclusive evidence on this point, a specially designed arrangement for the

* J. J. Thomson, 'Rays of Positive Electricity,' p. 112 (1913).

† F. W. Aston, 'Phil. Mag.,' vol. 39, p. 449 (1920).

concentration of the luminosity would be required. The authors hope to investigate the matter further.

The spectrum of neon, excited in the usual way, has been examined in considerable detail by various investigators. More recently, Paschen* and Hicks† have independently carried out researches upon the classification and arrangement of the lines observed. Hicks finds that neon gives results analogous to those obtained with the other inert gases, except that it differs from these in not showing two different spectra according as the discharge is passed with or without a condenser in the circuit.‡ The neon spectrum is compounded of the red and blue spectra typical of the rare gases, the blue spectrum being completely analogous to the blue spectra of the other gases. In the red region, however, there appears to be an excess of red lines over the number to be expected from the atomic weight of neon and its position with respect to the other elements of the same group. Hicks finds parallel D, S, and F series in neon, which are all related by the linkages to be expected and by Watson's constant frequency differences. The separations and linkages to be expected for any element are dependent upon a constant, known as the *oun*, characteristic of the element, and accurately proportional to the square of its atomic weight. It would, therefore, seem that if neon contains either two isotopes or two separate elements of atomic weights 20 and 22, two sets of linkages would be obtained, giving different values of the *oun*. Hicks' classification of the lines and his calculation of the neon *oun* show no evidence of this and thus throw no light on the origin of the several critical velocities we have obtained.

Paschen found it possible to group nearly all the observed lines into series of the forms:—

1	1·5, $S_n - m$, P_n
2	2, $P_n - m$, D_n
3	2, $P_n - m$, S_n

Some of these follow the Ritz interpolation formula with great exactitude while others require a modification of the Ritz expression. The series of the type 1·5, $S_n - m$, P_n were found to tend towards limiting frequencies for which the corresponding potential differences, calculated from the relation $eV = hn$, were very nearly the same. These limits were not directly observed, but as most of the lines in the series fell within the measured part of the

* F. Paschen, 'Ann. der Physik,' vol. 60, p. 405 (1919).

† W. H. Hicks, 'Phil. Trans.,' A, vol. 220, p. 335 (1920).

‡ This is not in agreement with the results of Merton who found that neon resembled the other inert gases in this respect. T. R. Merton, 'Roy. Soc. Proc.,' A, vol. 89, p. 447 (1914).

spectrum, the values of the constants of the series could be ascertained from directly observed lines. One of the series which agreed accurately with the Ritz formula contained the expression (m, S_5) . From this series the value of S_5 was obtained and the limit $(1.5, S_5)$ of some of the series of the $(1.5, S_n - m, P)$ type was calculated. This limit was $39,887.610 \pm 0.05$, and the corresponding potential difference is equal to 4.92 volts. On the accepted view, a radiation and the corresponding ionisation are connected with the excitation of the first and last lines, respectively, of the particular series resulting from displacements of an electron from its normal orbit. There must, therefore, be a series corresponding to displacements starting from the first orbit to which an electron can be projected from the normal orbit. The limiting frequency of this series would be expected to correspond to the difference between the minimum ionisation potential difference and the minimum radiation potential difference, which was found in the present research to be $(16.7 - 11.8 =) 4.9$ volts. Paschen's results show that the spectrum of neon contains series having limiting frequencies corresponding to this potential difference. Thus, although there is no evidence available for the region of the spectrum which includes the frequencies calculated from the observed critical electron velocities, the existing spectroscopic evidence is in accord with the values we have obtained for the minimum radiation and minimum ionisation velocities. The interval between the second radiation velocity and the third ionisation velocity is equal to $(22.8 - 17.8 =) 5.0$ volts, which again agrees, within the limits of experimental error, with the potential difference corresponding to the limit of known series in the neon spectrum.

*The Absorption of Light by Elements in the State of Vapour :
Selenium and Tellurium ; Mercury, Zinc, Cadmium ; Phos-
phorus, Arsenic, Antimony.*

By Sir J. J. DOBBIE, F.R.S., and J. J. FOX, O.B.E., D.Sc.

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[PLATES 1-3.]

Apart from what can be learned from the study of their density, little is known as to the constitution in the state of vapour of those elements which are solid or liquid at ordinary temperatures. In a paper read before the Society early last year* we showed that interesting information on this subject can be obtained from the examination of the absorption spectra of sulphur. In the present paper we propose to give an account of the application of the method to other elements. Unfortunately, the number of elements which lend themselves to the purpose is small, being limited to those which do not attack silica at a high temperature and volatilise below 1300° – 1400° C., the temperature at which silica begins to soften. Those most suitable for examination, besides the members of the sulphur group, are the mercury group, comprising mercury, zinc, and cadmium, in which the molecules are known to be mainly monatomic at all temperatures above their boiling points, and the phosphorus group, comprising phosphorus, arsenic, and antimony, in which the molecules are tetratomic.

The apparatus and arrangements employed in the investigation were similar to those described in the paper on sulphur, except that the tubes were exhausted as completely as possible by the Sprengel pump.

Selenium and Tellurium.

The general character of the absorption exercised by selenium is shown in fig. 1. From an examination of this figure, it will be seen that there is an increase in the amount of the absorption from 510° C. up to about 650° C., from which point it diminishes up to 850° C. Above 850° C., no further change is observed even at the highest temperature reached in our experiments, viz., 1350° C. These changes in the absorption spectrum can be followed readily by the changes of colour observed when the light, after passing through the vapour, is allowed to fall upon a white screen. The vapour is seen to become pale yellow almost suddenly at 600° C.; between 600° C. and 700° C. it is deep orange, and at this temperature it is almost

* 'Roy. Soc. Proc.,' A, vol. 95, p. 484 (1919).

opaque to the rays of the Nernst lamp. About 850°C . the colour has again become pale yellow, and no further change takes place at higher temperatures. A remarkable feature of these changes is the narrow range of temperature within which they occur.

The spectrum of selenium shows many narrow and sharp absorption bands, and presents generally the same channelled character as the spectrum of sulphur.

From the boiling point up to 900°C . the density of selenium vapour diminishes. At this temperature it corresponds closely with the formula Se_2 , and, according to Biltz,* this is still the molecular constitution at 1800°C . This agrees with our observation that there is no change in the absorption between 850°C . and 1350°C . According to Preuner and Brockmüller,† who deduced the molecular complexity from measurements of the vapour pressure carried out with a spiral quartz manometer, the selenium molecule approaches Se_6 at the lowest temperature of their observations, and Se_2 at the highest. At intermediate temperatures, intermediate values were obtained, the larger molecules, Se_6 , appearing to break down gradually into the smaller molecules, Se_2 . The vapour densities, which have been observed below 900°C ., are all greater than are required by the formula Se_2 . Determinations have been made by Szarvasy‡ at 918°C ., 898°C ., 815°C ., and 774°C ., at which the densities referred to air were found to be 5.60, 5.83, 6.63, and 7.01 respectively. When these results are plotted out, they are seen to lie on a straight line, which, when produced (see fig. 2), gives at 700°C . a density of 7.7, and at 650°C . a density of 8.2, the latter corresponding exactly with Se_3 .

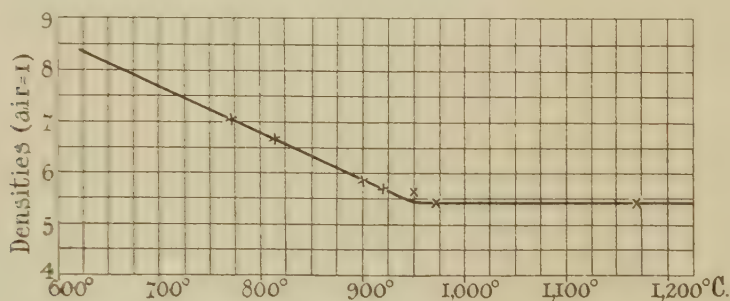


FIG. 2.

This temperature is very near the temperature of maximum absorption, which, as will be seen from the photograph (fig. 1), lies in the region of

* 'Zeit. physikal. Chem.,' vol. 19, p. 415 (1896).

† 'Zeit. physikal. Chem.,' vol. 81, p. 129 (1912).

‡ 'Ber. Deut. Chem. Ges.,' vol. 30, p. 1244 (1897).

650° C. to 700° C. There is thus close correspondence between the absorption curve and the vapour density curve so far as the data allow of the comparison being made. The point of maximum absorption of selenium lies very near that of sulphur, viz., 650° C., and strangely enough, as in the case of sulphur, the vapour density at that temperature corresponds with an average value of 3 atoms per molecule. It is also remarkable that both elements become wholly diatomic about 900° C.

The behaviour of tellurium is very similar to that of selenium, but owing to its much higher point of volatilisation, observations could be made only over a comparatively short range of temperature. From fig. 3 it will be seen that the general absorption increases with rise of temperature up to about 1250° C., after which it diminishes up to 1350° C. The light transmitted, which is pale yellow at the lower temperatures at which observations were made, becomes deep red at 1250° C., and again pale yellow at 1350° C. The spectrum is channelled like that of selenium. The only recorded vapour densities of tellurium were made at high temperatures. According to Biltz* the density at 1750°–1800° C. is 9.13, a value which corresponds nearly with the formula Te_2 . At high temperatures, therefore, the vapour of tellurium is undoubtedly composed mainly, if not entirely, of diatomic molecules, but in view of its similarity in behaviour to sulphur and selenium as regards the absorption of light, it may with great probability be inferred that, as in the case of these elements, its molecules are more complex at 1250° C. and lower temperatures than at 1750° C. At 1250° C. the constitution of its vapour would appear to be analogous to that of sulphur and selenium at 650° C.

On examining the photographs showing the absorption phenomena of the three elements of the sulphur group, it is seen that in order to obtain comparable results, the greater the atomic weight, the smaller is the quantity of the element that must be employed. In other words, the power of absorption increases with the atomic weight, and this we shall show in a future paper holds good also for the chlorine group.† With 8 mgrm. of tellurium the whole of the visible spectrum is cut out under the conditions of our experiments, whereas in the case of sulphur this is a very convenient quantity to employ in studying the absorption spectrum.

The following is a list of the principal absorption bands observed with the vapours of selenium and tellurium throughout the whole range of temperature employed:—

Selenium.— λ 5368*f*, 5299*f*, 5158*f*, 5136*w*, 4988*w*, 4972*w*, 4906, 4885*w*,

* 'Ber. Berlin Akad.,' p. 63 (1896).

† See also Mrs. Laird, 'Astrophys. J.,' vol. 14, p. 85 (1901).

4867*f*, 4844, 4815*w*, 4806, 4793, 4756*f*, 4726*w*, 4703, 4693, 4668, 4655, 4637, 4614*f*, 4590, 4557, 4528, 4504*w*, 4484, 4465, 4435, 4349*f*, 4304*f*, 4281*f*, 4242*f*, 4192*f*, 4179*f*, 4158, 4131, 4109, 4089, 4072, 4051, 4025, 4010*f*, 3988, 3976, 3955, 3937, 3920, 3899, 3878, 3868, 3841, 3834, 3820, 3810, 3790, 3778, 3765, 3755, 3743, 3734, 3723, 3712, 3703, 3690, 3678, 3667, 3655, 3627*f*.

The bands from λ 4435 to the red end of the spectrum are those of Se_2 since these occur at 900°C . and higher, at which temperatures selenium vapour is diatomic.

Tellurium.— λ 6331, 6316, 6284, 6259, 6220, 6201, 6180*w*, 6135*w*, 6115*w*, 6077*w*, 6046*w*, 6026, 6015*w*, 5968, 5951*w*, 5931, 5921, 5912, 5884, 5853*w*, 5830, 5797*w*, 5761*w*, 5748*w*, 5710*w*, 5701, 5689*w*, 5672, 5656*w*, 5639, 5624, 5614, 5581, 5565, 5550, 5528, 5504, 5489, 5466, 5451, 5439, 5426, 5415, 5399, 5389, 5369, 5358, 5347, 5329, 5316, 5308, 5295*w*, 5288, 5280, 5271, 5259, 5244, 5218, 5210, 5204, 5192, 5180, 5171, 5150, 5135, 5121, 5110, 5103, 5089, 5079, 5058, 5049, 5038, 5026, 5015, 5005, 4995, 4985, 4974, 4965*w*, 4956, 4947, 4937, 4926, 4901, 4888, 4879, 4863, 4844, 4834, 4817, 4802, 4794, 4783, 4774, 4760, 4745, 4735, 4723, 4716, 4709, 4698, 4687, 4675, 4664, 4646, 4639, 4629, 4619, 4602, 4590, 4578, 4568, 4559, 4546, 4537, 4526, 4519, 4512, 4505, 4498, 4491, 4485, 4478, 4469, 4459, 4451, 4440, 4428, 4419, 4411, 4400, 4391, 4380, 4373, 4367, 4360, 4348, 4340, 4330, 4321, 4312, 4303, 4294, 4284, 4275, 4266, 4256, 4246, 4236, 4227, 4220, 4211, 4204, 4190, 4179, 4162, 4142, 4134, 4114, 4106, 4086, 4062, 4041, 4024, 4018, 4006*w*, 3996, 3981, 3962, 3945, 3931, 3924, 3910, 3893, 3878, 3865, 3851, 3837, 3825.

The band at λ 4006 is the widest of this series of tellurium bands. Tellurium also exhibits a very wide area of absorption, the middle of which occurs about λ 4000 (fig. 4).

In the above list, *f* denotes a faint band, and *w* a wide band, the values shown in the latter case being the centre of the bands, which as a rule were of unequal sharpness at the edges.

Mercury, Zinc, Cadmium.

With a tube 100 mm. long and 12.5 mm. internal diameter containing 25.6 mgrm. of the metal, mercury showed no absorption at any temperature, the whole of the spectrum of the Nernst filament, which reaches to about λ 3100, being transmitted unaltered; with 46.6 mgrm. there was a slight absorption extending to about λ 3200, but very little further increase in absorption was observed when a tube 200 mm. long containing 105.8 mgrm.

was employed. The results were the same at all temperatures between 370° C. and 1300° C.

Cadmium (figs. 5 and 6), like mercury, shows no general absorption at any temperature, even with so large a quantity as 22.2 mgrm., but a small number of sharply defined absorption bands occur in the ultra-violet region of the spectrum in the following positions:—(a) A very fine sharp band at λ 3793, which shows at a temperature of 900° C. (b) A fine band at λ 3260 or λ 3261, showing first about 600° C., which widens as the temperature is raised; the widened band is sharp towards the red end, but shades off towards the ultra-violet. It coincides in position with the strong line of the cadmium arc at λ 3261.1. (c) A diffuse band at λ 3186, showing first at 900° C. (d)* Two sharp bands at λ 3654 and λ 3699, showing first about 1200° C. (e)* λ 3061, appearing at 1000° C., and λ 3382, appearing at 1100° C.

As it seemed possible that some of these bands might be due to impurities, great pains were taken to obtain the metal in the highest state of purity. Samples from American and German sources and samples prepared in the Government Laboratory by electrolytic deposition from acid solutions were all found to give identical results, and we conclude, therefore, that the bands are those of cadmium and are not due to impurities.

Zinc behaves generally in the same way as mercury; with 17.8 mgrm. no general absorption was observed at any temperature between that of volatilisation and 1300° C. At 1100° C. four very sharp faint bands make their appearance at λ 3699, λ 3654, λ 3384, and λ 3284. The zinc employed was the purest that could be obtained, and was free, so far as chemical tests showed, from all other metals except traces of lead and cadmium amounting to 0.016 per cent. and 0.005 per cent. respectively. Such minute quantities are, so far as our experience goes, without effect on the absorption spectra.

Considered as a group, these elements differ widely from sulphur and resemble each other in that: (1) they are transparent to light as far as the spectrum of the Nernst filament extends, that is, to about λ 3100; (2) increase of temperature is not accompanied by the peculiar behaviour exhibited by sulphur, viz., increase of absorption followed by decrease as the temperature is raised; (3) increase in the quantity of the element within the limits of our experiments has little influence upon the spectrum. The results obtained with 46.6 mgrm. of mercury are much the same as with more than double that quantity; with 10.4 mgrm. of cadmium the same as with 22.2 mgrm., and with 17.8 mgrm. of zinc the same as with 28.4 mgrm.

* These lines are not shown in the reproduction, although clearly marked on the original negatives.

Phosphorus, Arsenic, Antimony.

Phosphorus, arsenic, and antimony, which are known from their vapour densities to be tetratomic, behave differently from the elements of the other groups already examined. With 9.4 mgrm. of phosphorus heated from 420° C. to 1310° C. the spectrum, which extends to λ 3300 at the lower temperature, gradually contracts as the temperature is raised, until at the highest temperature reached it only extends to λ 3730. With 13.6 mgrm. the result is similar, the only difference being that the amount of absorption is greater, the spectrum only reaching to λ 3400 at 420° C. and to λ 3950 at 1310° C. The phosphorus, it may be mentioned, was introduced into the tube in the red or amorphous form.

Arsenic shows similar phenomena to phosphorus. Between 400° C. and 1320° C. (fig. 7) there is a regular increase in the general absorption, the spectrum being transmitted to λ 3250 at 400° C. and to λ 4440 at 1320° C. When the amount of arsenic is increased, the only effect is to increase the amount of absorption at corresponding temperatures. The absorption extends in this case into the visible region of the spectrum and the colour of the arsenic vapour becomes faintly yellow at 700° C., deepening as the temperature is raised.

On account of the higher temperature required to volatilise antimony, this element could only be examined over a comparatively short range of temperature, viz., 800° C.–1300° C., but it will be seen from fig. 8 that between these temperatures it behaves in the same way as phosphorus and arsenic. With 31.6 mgrm. the spectrum is transmitted to λ 3150 at 800° C. and to λ 4000 at 1300° C. The antimony used was prepared from tartar emetic.

It may here be mentioned that in dealing with elements which require a high temperature for volatilisation it is found most convenient to heat the tube to the highest temperature to begin with, and take the photographs as the temperature falls, so as to ensure that the whole of the contents of the tube are in the state of vapour during examination. The deposition of any of the elements in the solid state is at once indicated by the light being partially or entirely cut off by obscuration of the end plates.

It is well known that the density of the vapour of phosphorus, arsenic, and antimony diminishes with increase of temperature. It may, therefore, be assumed that, as in the case of sulphur, the increase of absorption which takes place when the temperature is raised is closely associated with the breaking down of the more complex molecules. No absorption bands or indications of any kind of selective absorption were observed in the elements of this group.

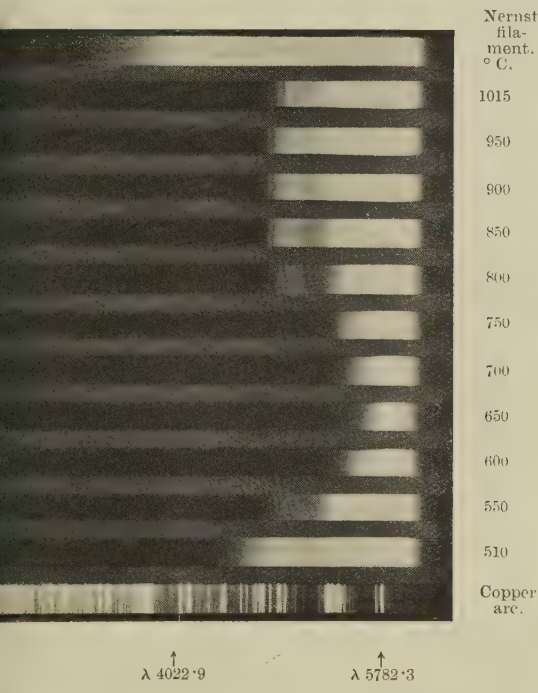


FIG. 1.—Spectrum of 4.3 mgrm. of Selenium.

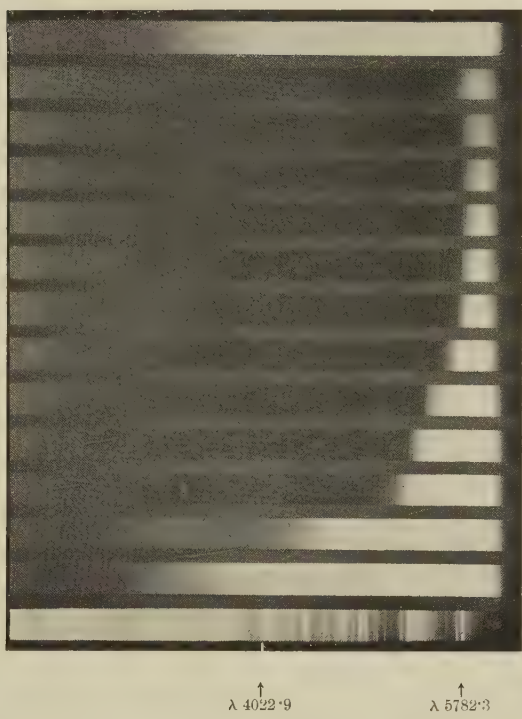


FIG. 3.—Spectrum of 4.9 mgrm. of Tellurium.

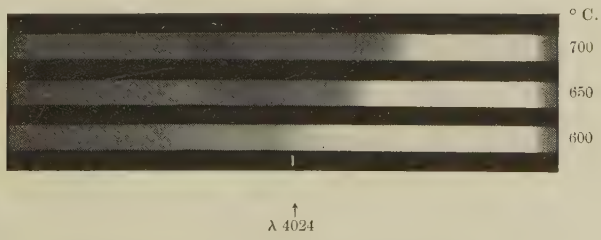


FIG. 4.—Spectrum of 0.4 mgrm. of Tellurium.

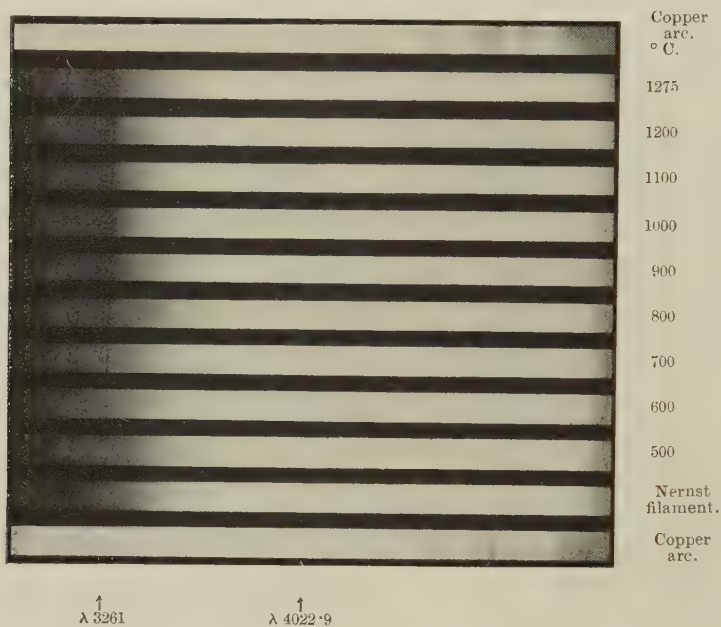


FIG. 5.—Spectrum of 22.2 mgrm. of Cadmium.

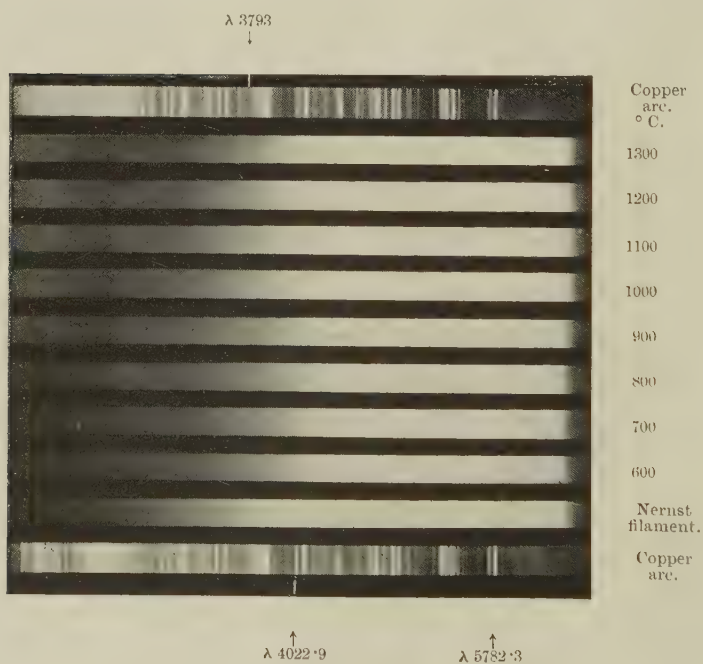


FIG. 6.—Spectrum of 21.6 mgrm. of Cadmium.

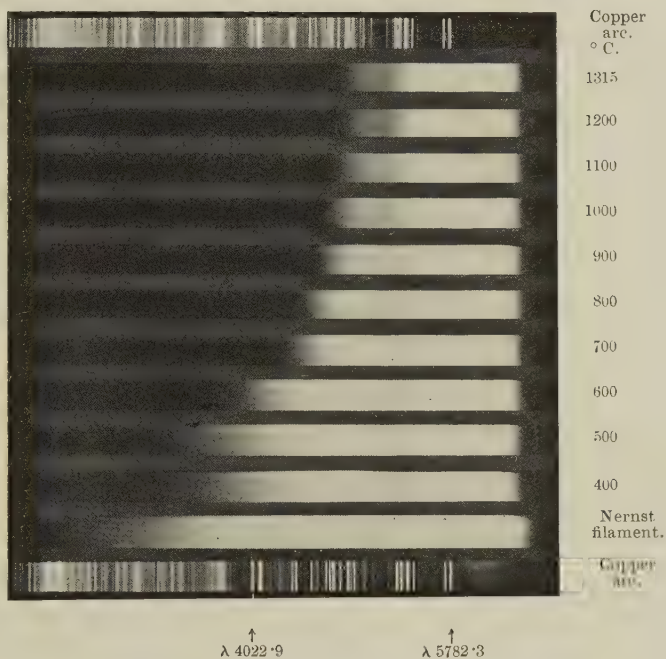


FIG. 7.—Spectrum of 24.6 mgrm. of Arsenic.

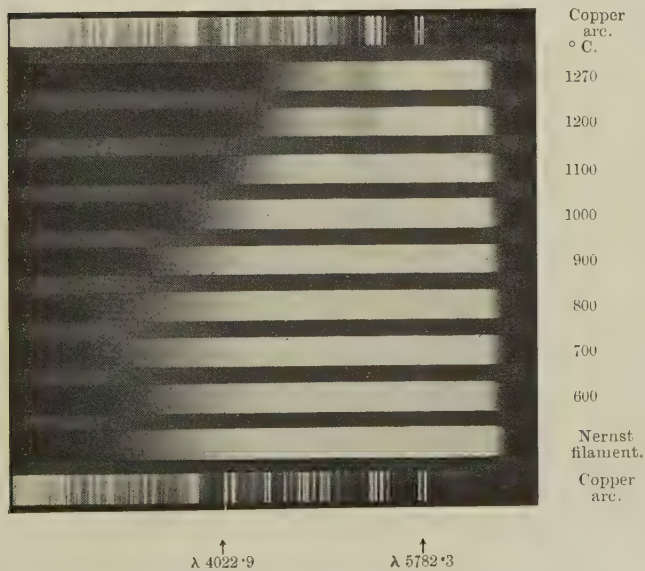


FIG. 8.—Spectrum of 31.6 mgrm. of Antimony.

Where the absorption of light increases with increase of temperature there is evidence of the resolution of more complex into simpler molecules; where there is no increase of absorption there is evidence that the element is monatomic in the gaseous state. In the case of mercury the evidence, based on several distinct methods of investigation, points to the conclusion that the vapour consists entirely of molecules composed of single atoms. The vapours of zinc and cadmium have densities which indicate that their molecules also for the most part consist of single atoms. The discrepancy, however, between the vapour density, calculated on the assumption that these two elements are monatomic, and that actually observed even at high temperature shows that the molecules in the gaseous state do not *wholly* consist of single atoms. The fine bands described above may well be connected with the presence of the more complicated molecules.

Bearing in mind the results previously obtained with sulphur, it would appear that the elements which lend themselves to examination by the method described in this paper may be divided into three groups:—

(1) Elements whose vapours exercise no absorption or show only a few well-defined absorption bands: these are monatomic.

(2) Elements in which the absorption gradually increases as the temperature is raised, but which show no other effect within the limits of temperature imposed by our method: these are tetratomic.

(3) Elements in which the absorption increases with increase of temperature to a maximum and afterwards diminishes. The sulphur and halogen elements belong to this group.

The explanation of the different behaviour as regards absorption of light, as exhibited by elements of groups (2) and (3) compared with those of group (1), is probably to be found in the rearrangement of the valencies accompanying the breaking down of the complex molecules under the action of heat. The tetratomic molecules would appear to break down simply into diatomic molecules, although possibly more complicated changes may take place at higher temperatures than can be employed with silica tubes. With the sulphur and halogen elements, the changes are obviously much more complex. The molecules near the temperature of volatilisation are probably already broken down, partially to the atomic condition, the liberated atoms forming new combinations with one another or with the undissociated molecules, in other words, polymerising. This subject will be more fully discussed in a future communication on the elements of the halogen group, which we are at present investigating.

Photochemical Investigations of the Photographic Plate.

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(Communicated by Prof. J. N. Collie, F.R.S.—Received June 26, 1920.)

[PLATE 4].

Introduction.

Many theories of the latent image and of the means by which light impressions are produced in the photographic plate have been developed from time to time, but most of these theories are so indefinite that they cannot be tested experimentally, and are of no use in forecasting what will happen under fixed conditions. A quantitative theory was put forward by Hurter and Driffield,* and their theory was further advanced by Channon.† Some of the difficulties inherent in this theory have been pointed out by Bloch and Renwick‡ and by Channon, Renwick, and Storr.§ There is no need to go into details of this theory of Hurter and Driffield, as the experiments described below show that two of their fundamental assumptions are not true.

The gelatine dry plate consists of a skin or pellicle of dried gelatine, containing particles of silver bromide or a mixture of silver bromide and silver iodide. The average commercial plate contains about 0.2 gramme of gelatine and 0.1 gramme of silver bromide per square decimetre of surface. On such plate the coating of dried gelatine is about 25 microns (micron = μ = 0.001 mm.) thick, and if the plate is a process plate containing grains about 0.7μ in diameter, there will be about three and a half layers of grains in the coating. If it is a fast plate with grains varying in size up to 2μ or 3μ , it will contain only one to two layers of particles. These layers are of course distributed at random through the film.

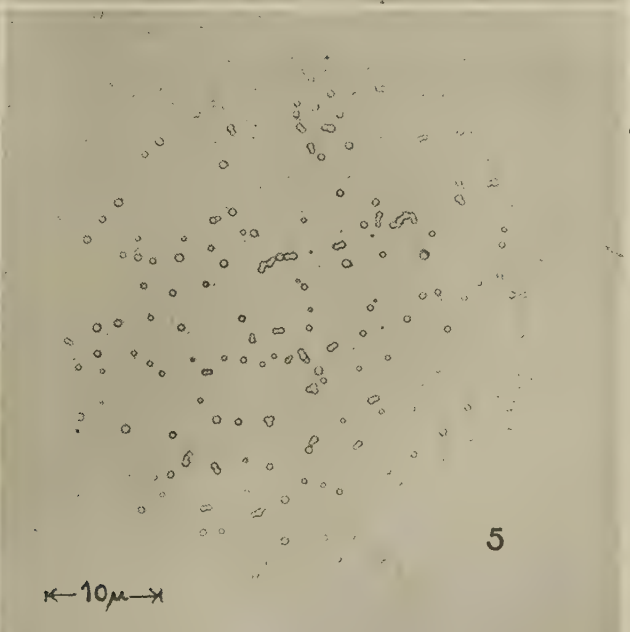
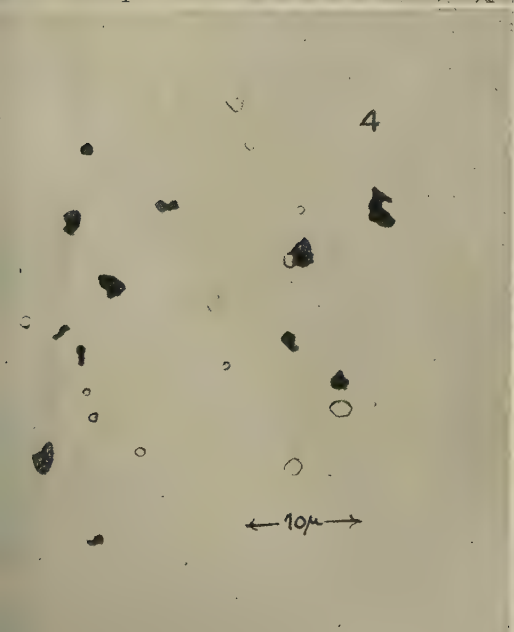
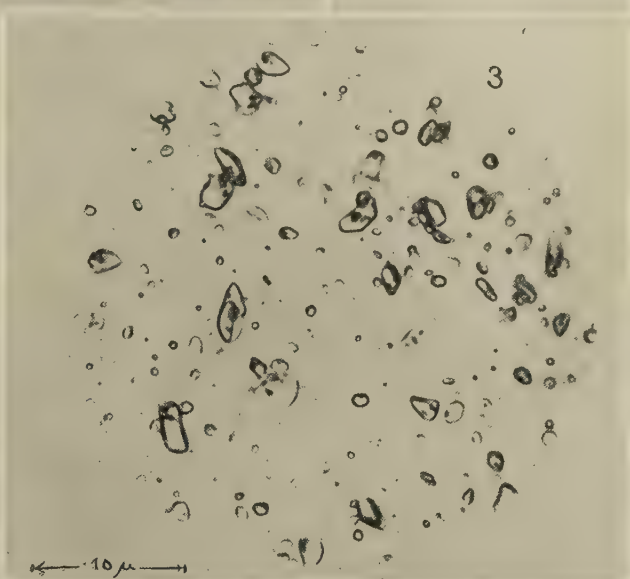
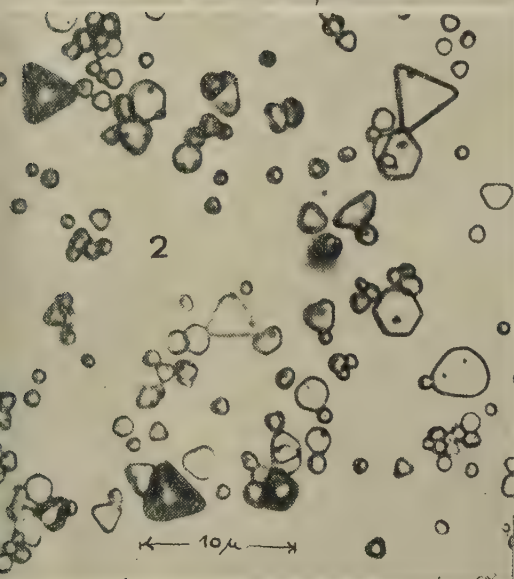
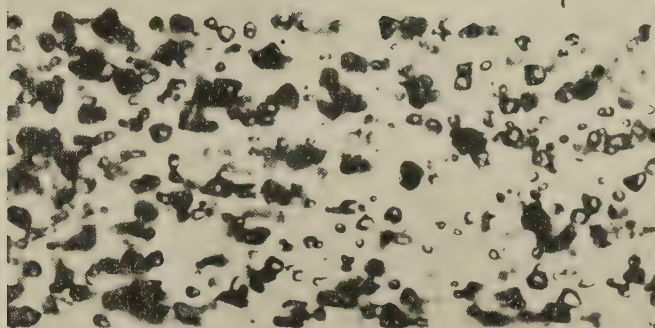
Fig. 1, Plate 4, is a photomicrograph of a section of a photographic film, cut at right angles to the surface, the section being cut with a microtome without embedding in any way. The layer of emulsion as seen in fig. 1 is in exactly the same state as it would be when exposed in the camera. Unfortunately, it has not been possible to cut a section of thickness equal to the diameter of a single grain. The section in fig. 1 is probably about 10μ or 15μ thick, so that many of the particles are out of focus. If a straight line

* 'Jour. Soc. Chem. Ind.,' May 31st, 1890.

† 'Phot. Jour.,' vol. 46, p. 216 (1906).

‡ 'Phot. Jour.,' vol. 56, p. 49 (1916).

§ 'Phot. Jour.,' vol. 58, p. 121 (1918).



were drawn through the film shown in this figure, perpendicular to the surface at any point, it would only cut through two or three particles.

Silver bromide crystallises at ordinary temperatures in the regular system in the form of cubes, but if the crystals are grown in the presence of gelatine, as in emulsion-making, they assume the form of triangular or hexagonal plates, tetrahedra, or crystals with curved faces. Silver bromide and silver iodide together form mixed crystals in the cubic system, even at ordinary temperatures.* Figs. 2 and 3 are typical photomicrographs of the crystals existing in photographic plates. When the crystals are less than $0.8\ \mu$ across, it is impossible to say whether they are crystalline or not, but since there is, so far as is known, perfect continuity in the properties of plates containing particles varying from ultramicroscopic dimensions to $2\ \mu$ or $3\ \mu$, and, as the latter particles are most certainly crystalline, it seems legitimate to assume that the smallest particles are also crystalline.

Preliminary experiments have shown that the grain or crystal of silver halide is the photochemical unit in the gelatine dry plate.

A plate is coated with a very thin layer of photographic emulsion, so that the gelatine film in it contains only one layer of grains and the plate is then, after drying, exposed to light for a time insufficient to make all the particles developable. If the plate is then developed, washed, and dried without fixing and examined in the microscope, it is found that some of the grains have become changed to silver while others are unaffected. The appearance of such a plate is shown in fig. 4. It therefore seems reasonable to assume that each grain acts quite independently and that one grain which has become developable is unable to make a grain, situated in close proximity to it, developable unless the latter grain is developable in itself. This is clearly shown in fig. 4. If this thinly coated plate is exposed to light for a longer time or to light of greater intensity, more and more of the grains are made developable. It is therefore obvious that the grain or crystal of silver halide is the photochemical unit in the gelatine dry plate, and a theory of the photographic plate can only be built up on a knowledge of the photochemical behaviour of the single grain of silver halide. The photochemical law of the silver halide grain was therefore made the subject of the present investigation.

The blackening obtained on development of a photographic plate which has been exposed to light of a given intensity for a given time is determined by the following factors:—

(I) The Photochemical Law of the Silver Halide Grain, that is, the law

* Thiel, 'Zeit. f. anorganische Chem.,' vol. 24, p. 1 (1900).

determining the relation between P , the probability of a single grain being made developable in unit time, and t , the time of exposure, and I , the intensity of light to which the grain is exposed, *i.e.*, the form of the equation $P = f(I, t)$.

(II) If the grains are not all the same in size and quality, there will be a law for each set of identical grains. (All experimental evidence leads to the conclusion that all grains in one emulsion behave identically if they are of the same size.)

(III) If the silver halide absorbs actinic light the intensity of such light will fall off as it passes through the coating on the plate, so that the back layers of the silver bromide particles will be exposed to much weaker light than the front layers. The light gradient through the film will depend on (a) the absorption of light by the silver bromide, (b) the relative refractive indices of the grains and of the gelatine which determine reflexion, (c) the closeness of packing of the grains.

(IV) Development consists in reducing to metallic silver, either wholly or partially, those grains which have been made developable by light. Since different developers act at different rates (also varying with the temperature) and diffuse at different rates into the gelatine layer, and as the state of dispersion of the silver formed varies to some extent with the developer used, the blackening must be affected by the developer. But it has been shown by Hurter and Driffield, Sheppard and Mees, and others that for a given plate and a given developer the photometric density is proportional to the amount of metallic silver in the film.

From the experiments mentioned above, and from the work of others, especially Luther,* it appears that when a grain of silver halide becomes developable there is formed in it a nucleus which is effective in causing development to take place. It should be remembered that the function of gelatine during development is to make development of grains which have not been affected by light extremely slow. If gelatine or some similar substance is not present, all grains exposed or unexposed develop equally well.

If (following Einstein) it is assumed that light is discrete in its nature, and that it is only necessary for one of these light quanta to be absorbed by a grain to make it developable, then if there were a number of grains, a , present on the plate, and they were exposed to a light of intensity, I , for a time, t , after which time x grains had been made developable,

$$\frac{dx}{dt} = kI(a-x)$$

* 'Zeit. phys. Chem.,' vol. 30, pp. 628, 652 (1899).

and integrating between limits 0 to t and 0 to x

$$\log_e \frac{a}{a-x} = kIt,$$

or

$$x = a(1 - e^{-kIt}).$$

If the grains were of different sizes, the probability of their obtaining a nucleus would vary, the larger grains being more likely to be affected; k would therefore have a different value for each size of grain.

The present investigation has shown that k has a larger value for larger grains, but also that it is not generally true that the number of grains changed is a simple function of the product It . *It is therefore impossible that the mechanism of the process is the absorption of light in discrete quanta, as has been assumed above.*

In this investigation of the photochemical law of the silver halide grain, plates were prepared from an emulsion containing grains which were, as nearly as possible, all the same size. The emulsion was coated on the plate in such a thin layer that there was only one layer of grains. These plates were exposed either to varying intensities for the same time or to the same intensity for varying times. The source of light used was monochromatic blue light from the mercury arc in some cases, and white light (continuous spectrum) in others.

If the total number of grains present is a , and x is the number changed after exposure for a time, t , to a light of intensity, I , then

$$\frac{dx}{dt} = P(a-x),$$

where P is the probability of any grain being made developable in unit time, and is a function of I and of t .

Integrating
$$\int_0^x \frac{dx}{a-x} = \int_0^t P \cdot dt,$$

therefore
$$\log_e \frac{a}{a-x} = \int_0^t P \cdot dt.$$

This, however, does not make it possible to evaluate P as a function of I and t without making other assumptions.

The experimental values of this integral will now be considered, and afterwards the assumptions which it is necessary to make to obtain a relation between P , I , and t , which shall be in agreement with experimental facts, will be discussed.

Experimental.—In order to investigate factor (I) (the Photochemical Law of the Silver Halide Grain), the other three factors have been eliminated in the following manner. The plates which were used were coated with such a

thin layer of emulsion that there was only a single layer of grains on the plate; this eliminates factor (III). In the emulsion used to coat these plates all the grains were of the same size, and experimental proof has been obtained that they were all of the same quality; this eliminates factor (II).

Fig. 5 is a photomicrograph of the emulsion and shows that the grains were about $0.8\ \mu$ in diameter and were practically all the same size.

The plates were exposed to light under various controlled conditions, developed to infinity in a restrained developer (which does not develop unexposed grains in a reasonable time), washed and dried without fixing. They were then examined with the microscope and the total number of grains present in a given area and the number which had been blackened by development were counted. It was found that, for the same exposure, the fraction of the total number of grains which were blackened was for the same plate independent of the developer used; this eliminates factor (IV).

Preparation of Plates with One Layer of Halide Grains.—A commercial process plate having all the grains of one size was chosen. In non-actinic light the emulsion on one quarter-plate was dissolved in 100 c.c. of 5 per cent. gelatine solution at 40°C . Glass slips, 4 inches by 1 inch, were coated by dipping them into the dilute emulsion (kept at 40°C .), shaking off the superfluous liquid and drying them in a current of cold dry air. The plates are thus, of course, coated on both sides. One side is then coated with red backing paper, to absorb light which would otherwise be reflected from the back of the plate.

Development.—After exposure, the plate was developed for three minutes at 18°C . in a developer composed of amidol 0.4 gm., Na_2SO_3 3 gm., KBr 2.5 gm., water 100 c.c. This developer has no effect on unexposed grains in five minutes at 18°C ., but completely develops the exposed grains in three minutes. The plate was next thoroughly washed in the dark, and then dried without fixing.

Determination of the Number of Grains Developed.—The plates were examined visually in the microscope, and the number of changed (black) and unchanged (transparent) grains in a given area counted. The appearance of such plates in the microscope has already been shown in fig. 4. The area in which the number of grains was counted each time was $60\ \mu$ by $72\ \mu$, i.e., 0.0043 sq. mm., and usually contained from 200 to 500 grains, according to the coating of the emulsion.

If the exposed and unexposed grains are distributed entirely at random over the surface of the plate, from the law of probability can be calculated the average error, in assuming that the percentage of each present is equal to the percentage obtained by counting a finite number of grains.

If N is the number of events, and p and q are the probabilities of the two events, P and Q , happening, the average error, E , is given by the equation

$$E = \pm \sqrt{Npq};$$

whence the percentage error

$$= \frac{100E}{N} = \pm 100 \sqrt{\frac{pq}{N}}.$$

In the counting of the grains, the number of events, N , is the number of grains counted, and p and q are the fractions of the total number which are changed and unchanged respectively. That is, $p+q=1$ or $q=1-p$. The following values of the percentage error have been calculated from the values of N and p :—

Number of grains counted.	Percentage of grains changed.	Percentage error.
100	50	± 5
200	50	± 3.5
300	50	± 2.9
500	50	± 2.2
1,000	50	± 1.6
10,000	50	± 0.5

Number of grains counted.	Percentage of grains changed.	Percentage error.
324	2 or 98	± 0.8
324	5 95	± 1.2
324	10 90	± 1.7
324	20 80	± 2.2
324	30 70	± 2.6
324	40 60	± 2.7
324	50	± 2.8

As a rule, about 500 grains were counted, which reduces the error to a reasonable figure without necessitating the counting of an excessive number of grains.

Effect of Different Developers.—The following experiment shows that the fraction of the total number of grains blackened after a given exposure was independent of the developer used, so long as the developer was sufficiently restrained to prevent fogging during the time of development.

A thinly coated plate was exposed to light, so as to change about 80 per cent. of the grains. It was then cut in half, and the two halves were developed at 18° C. for about three minutes in (A) amidol and (B) metol-hydroquinone respectively, and finished in the way described above. The numbers of the unchanged and blackened grains were then counted on

widely separated portions of each half. The following results were obtained:—

Number of grains counted.	Number of blackened grains.	Percentage blackened.
A (Amidol developer).*		
178	143	80.4
206	170	82.5
204	166	81.4
181	144	79.6
769	623	81.0
B (Metol-hydroquinone developer).†		
238	190	79.9
215	168	78.2
161	134	83.2
204	164	80.4
188	149	79.3
215	176	81.9
189	151	80.0
1410	1132	80.4

* As given above.

† Metol-hydroquinone developer:—Metol 0.1 grm., hydroquinone 0.4 grm., Na_2SO_3 1.8 grm., Na_2CO_3 1.4 grm., KBr 2.6 grm., water 100 c.c.

It will be seen that the values 81.0 and 80.4 per cent. are in as good agreement as could be expected from the probability theory, for the average percentage error on the 81.0 per cent. would be

$$100 \sqrt{\frac{0.8 \times 0.2}{769}} = \pm 1.4 \text{ per cent.},$$

and the average percentage error on the 80.4 per cent. would be

$$100 \sqrt{\frac{0.8 \times 0.2}{1410}} = \pm 1.1 \text{ per cent.}$$

Similar results were obtained with other developers.

The Form of the Function $P = f(I, t)$.

(1) *The Determination of the Effect of Variation of Light Intensity, the Time of Exposure being Constant ; $[P]_t = f(I)$.*

In these experiments, the thinly coated plates were exposed to monochromatic blue or to white light behind a Goldberg neutral wedge. This

wedge consisted of a dried pellicle of gelatine, containing finely divided carbon, mounted between two sheets of glass.* The opacity increased from the thin end in such a way that, if two points, R and S, were distant r and s cm. from the thin end of the wedge, then if the wedge was evenly illuminated, the intensity transmitted at R equalled $(s-r)$ (2.046) times the intensity at S. It was therefore possible to determine the relative intensity to which any part of the plate had been exposed. The constant of the wedge was determined by measurement in a spectrophotometer. The wedge has been found to be quite neutral over the range of wave-lengths used, and in this respect the Goldberg wedge is much better than any "neutral" glass wedge which has been prepared up to the present.

Monochromatic blue light was obtained by filtering the light from a mercury arc through two filters, one consisting of a gelatine film dyed with methyl violet, and the other of a solution of cupric chloride in saturated potassium chloride. Precautions were taken to ensure that the wedge was always evenly illuminated, and that the time of exposure was the same all over the wedge. In different experiments, the intensity incident upon the wedge was varied by altering the distance between the wedge and the light source. Where the incident intensity was great, the time of exposure was correspondingly less, so that there was always a portion of the plate (under the most opaque portion of the wedge) which had not been affected appreciably by the light.

The mercury arc burned steadily during any one particular experiment, but the energy used in the arc was only approximately the same in different experiments. Since the experiments are not strictly comparable with one another, owing to other variations in the conditions (*e.g.*, the speeds of two different batches of thin plates will never be exactly the same), this variability of condition is not important. In Experiments 1-5 the incident intensity is given in terms of Q , the intensity at 1 metre from the light source, with the blue filters in position. In Experiment 6 no filters were used, and therefore the intensity is in no way comparable with that in Experiments 1-5. In Experiments 6-10 white light was used. From the values of x thus obtained, the values of $\log_e \frac{a}{a-x}$ (which will be denoted by A) were calculated, as this has been shown above, to be equal to

$$\int_0^t P \cdot dt = \int_0^t f(I, t) dt.$$

* Goldberg, 'Brit. Jour. Phot.', vol. 57, p. 648 (1910).

Intensity Scale Experiments.

Experi- ment No.	Distance from light source in metres.	Incident intensity.	Time of exposure.	Intensity on plate (in "Q").	Percentage of grains changed.	A.
Monochromatic Blue Light.						
1	1	Q	5 secs.	0.489	45.7	0.61
				0.239	23.5	0.27
				0.117	9.2	0.10
				0.0570	7.0	0.07
				0.0279	2.9	0.03
				0.0136	1.0	0.01
2	0.5	4 Q	5 secs.	0.951	70.0	1.20
				0.465	52.5	0.74
				0.227	31.5	0.38
				0.111	13.9	0.15
				0.0542	7.5	0.08
				0.0265	2.1	0.02
3	1	Q	1 min.	0.0129	0.6	0.006
				0.489	100 app.	
				0.239	99 app.	4.6*
				0.117	80.2	1.62
				0.0815	63.0	0.99
				0.0570	34.9	0.43
4	2	0.25 Q	10 mins.	0.0279	21.9	0.25
				0.0136	9.3	0.01
				0.00665	4.5	0.05
				0.00325	0.6	0.001
				0.0142	100 app.	
				0.00679	92 app.	
5	4	0.0625 Q	40 mins.	0.00498	70.4	1.22
				0.00340	39.1	0.50
				0.00166	11.2	0.12
				0.000813	5.8	0.06
				0.000568	4.3	0.04
				0.000398	2.6	0.027
				0.000224	0.5	0.005
				0.0306	100 app.	
				0.0149	87.0	2.04
				0.00730	41.0	0.53
				0.00357	10.5	0.11
				0.000851	5.3	0.05

Experi- ment No.	Distance from light source in metres.	Incident intensity.	Time of exposure.	Intensity on plate (Relative).	Percentage of grains changed.	A.
Mercury Arc Light.						
6	1	Very great	Fraction of sec.	0.478	96.4	3.33*
				0.229	78.0	1.31
				0.110	48.5	0.66
				0.0525	27.3	0.32
				0.0251	13.2	0.14
				0.0120	4.7	0.05
				0.00575	1.3	0.013
				0.00273	0.9	0.009
				0.00132	0.6	0.006

* Doubtful values.

Intensity Scale Experiments—*continued.*

Experiment No.	Distance from light source in metres.	Incident intensity in candle-metres.	Time of exposure.	Intensity on plate in candle-metres.	Percentage of grains changed.	A.
White Light (Continuous Spectrum).						
Illuminant: 100 c.p. Pointolite Lamp.						
7	0.25	1600	Less than 1 sec.	775	100 app.	
				378	100 app.	
				185	94.3	2.78
				90.4	71.9	1.27
				63.1	52.4	0.74
				44.2	31.2	0.38
				21.6	12.0	0.13
				10.5	4.6	0.05
				5.15	0.4	0.004
				2.52	Nil	Nil
Illuminant: 200 c.p. Half Watt.						
8	0.5	800	7 secs.	271	100 app.	
				190	99 app.	
				92.7	86.9	2.03
				45.3	68.0	1.14
				22.1	44.4	0.59
				10.8	16.9	0.19
				5.28	5.4	0.06
				2.58	1.1	0.01
				1.26	Nil	Nil
Illuminant: 16 c.p. Metallic Filament at 50 volts constant.						
9	0.83	23.2	22 secs.	13.0	97.6	3.75*
				11.4	93.6	2.21
				7.93	72.5	1.29
				6.62	46.3	0.62
				5.55	35.9	0.44
				3.88	22.0	0.25
				2.71	15.7	0.17
				1.32	6.5	0.07
				0.925	5.5	0.06
				0.647	3.9	0.04
				0.316	0.6	
				0.158	0.5	
				0.0378	0.4	
Illuminant: 16 c.p. Metal Filament Lamp at 50 volts constant.						
10	1.414	8	10 mins.	1.89	100 app.	
				0.927	100 app.	
				0.453	98 app.	3.91*
				0.316	80.0	1.61
				0.221	53.0	0.76
				0.108	15.0	0.16
				0.0528	5.3	0.05
				0.0258	1.7	0.02
				0.0126	0.8	0.01

* Doubtful values.

Figs. 6-12 show A plotted as a function of I and I^2 for some of these experiments. As A is obtained from the values of x by calculation, it is obvious that, when x becomes about 95 per cent., very small changes in x produce very large changes in A, which changes become infinitely great as x

approaches 100 per cent. Consequently, very small errors in x above 90 per cent. produce enormous errors in A , and values of A greater than 3 are most unreliable.

Nevertheless, it will be seen, from an inspection of the figures, that when I is great and t is small, $A = k_1 I$, and when I is small and t is great, $A = k_2 I^2$. A function which will give this is

$$[A]_t = k_1 I (1 - e^{-k_3 I}).$$

For when I is small $k_3 I$ is also small and

$$A = k_1 I \quad k_3 I = k_2 I^2,$$

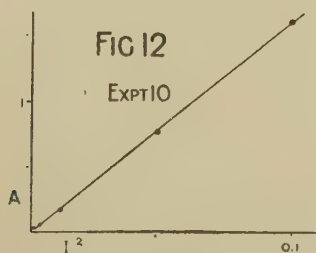
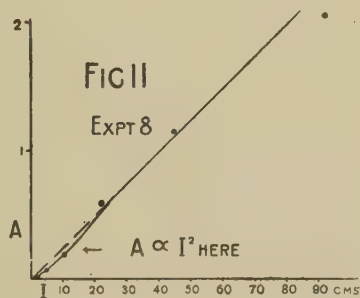
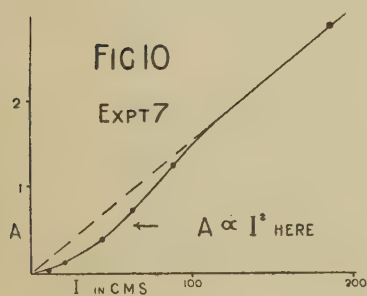
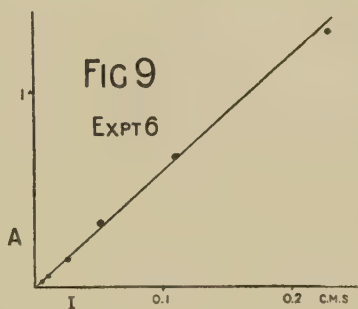
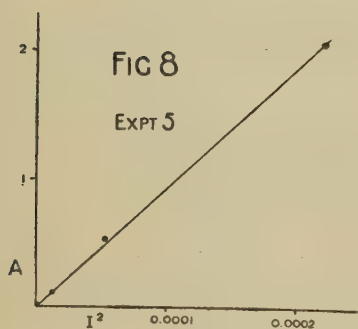
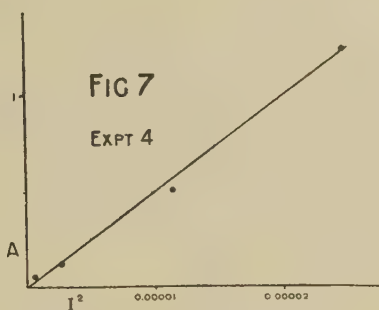
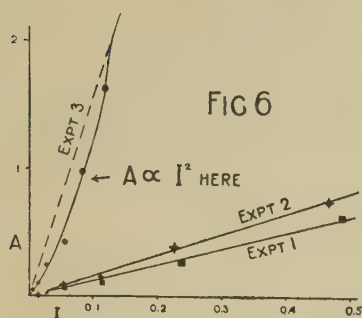
and when I is large $e^{-k_3 I}$ is small compared with unity, and therefore

$$A = k_1 I.$$

k_1 is, of course, a function of t , and of the size (*i.e.*, the speed) of the grains. k_3 has been found to be a function of the quality of the light. If the light is monochromatic, or concentrated in narrow bands, as in the mercury arc, k_3 is large; but, if the light is white (continuous spectrum), k_3 is small, and, therefore, for very much higher intensities, A is a linear function of I^2 . By higher intensity is meant an intensity that changes more grains in a given time. The above conclusions are easily drawn by references to figs. 6-12, and particularly by a comparison of figs. 6-8 with figs. 10-12.

Fig. 9 is a typical curve, with light from the mercury arc without a light filter, that is to say, with the blue line and all the lines of this arc of shorter wave-length affecting the plate. In this case the curves are somewhat similar to those obtained with monochromatic blue light. Figs. 10-12 show some curves obtained with a continuous spectrum, and it will be noticed that in these curves the change from A being a linear function of I , to A being a linear function of I^2 , does not take place at such an intensity that the time required to change half the grains (*i.e.*, when $A = 0.693$) is about one minute, as is the case with monochromatic blue light, but that all the curves show A a linear function of I^2 , even when the intensity is so great that the exposure to change half the grains is very short indeed.

The explanation of this phenomenon is probably that the width of the spectrum over which light energy collectively forms a quantum is very narrow. That is to say, using monochromatic light, all the energy is of the same kind, and therefore the number of quanta is $E/h\nu$, where E is the total light energy. But if the light is distributed over a continuous spectrum, and there are perhaps a thousand different regions of the spectrum which do



not reinforce one another, then, if the energy in each of these regions were the same, there would not be even one complete quantum formed until $1000 h\nu$ ergs had been absorbed, and then 1000 quanta would be completed at once. In actual cases, the energy varies in the different regions of the spectrum. *All these experiments show that the same amount of light energy is much less effective on the grains if it is spread over a range of the spectrum than if it is concentrated in one spectrum line.*

(2) *Determination of the Effect of Variation of Time of Exposure, Light Intensity being Constant.*

Since A is a function of both I and t , it is necessary to consider, along with the curves obtained by variation of intensity, those obtained by keeping the intensity constant and varying the time. This was found to be more difficult than the investigation of the intensity curves, as variation of time can only be obtained by some mechanical device, which may be the cause of additional errors. In the experiments which follow, the variation of time was obtained either by use of the ordinary H. and D. sector wheel exposure machine, or by a special apparatus designed for the purpose.* In both cases the exposure is non-intermittent, the non-intermittency of the special machine being inherent, and the same effect being obtained with the H. and D. machine by running it very slowly, and using only one revolution for an exposure, the largest interrupted sector not being used. This precaution is absolutely necessary, as it has been found during these experiments that intermittency has a marked disturbing effect.†

The illumination of a plate during exposure was subject to the same precautions as those taken in the first set of experiments (Experiments 1-10), and the development and counting of the grains, etc., were exactly similar. The following results were obtained, in which, as in (1) (Intensity Scale Experiments), Q denotes the intensity of the monochromatic blue light at a distance of 1 metre and A the probability integral

$$\int_0^t P \cdot dt = \log_e \frac{a}{a-x}.$$

* Higson, 'Phot. Jour.', vol. 60, p. 235 (1920).

† Cf. Jones, 'Phot. Jour.', vol. 60, p. 80 (1920).

Time Scale Experiments.

Experiment No.	Distance from light source in metres.	Intensity incident.	Time of exposure (secs.).	Percentage of grains changed.	A.
Monochromatic Blue Light.					
11	0·8	1·56 Q	3	95·5	3·11
			2	89·4	2·25
			1·5	70·6	1·22
			1	39·9	0·51
			0·5	14·4	0·16
12	1	1·56 Q	8	97·7	3·82*
			6	90·2	2·32
			5	80·3	1·62
			4	68·4	1·15
			3	36·2	0·45
			2	21·0	0·24
			1	10·8	0·12
13	2	0·25 Q	60	96·0	3·22
			50	90·7	2·44
			40	73·8	1·34
			30	62·1	0·97
			20	48·3	0·66
			10	30·5	0·37
			5	15·7	0·17
			2·5	7·6	0·08
14	3	0·111 Q	200	97·5	3·71*
			150	95·7	3·00
			100	93·5	2·74
			50	82·6	1·81
			40	75·6	1·41
			30	65·5	1·07
			25	44·8	0·59
			20	27·1	0·32
			10	2·1	0·02
15	4	0·0625 Q	600	64·5	1·03
			500	60·0	0·92
			400	57·4	0·85
			300	42·1	0·55
			200	32·5	0·39
			100	18·0	0·20

* Doubtful values.

Time Scale Experiments—*continued*.

Experiment No.	Distance from light source in metres.	Incident intensity, candle-metres.	Time of exposure in secs.	Percentage of grains changed.	A.
White Light.					
16 c.p. Metal Filament Lamp, running at 50 volts constant.					
16	0.6	44.5	10	94.5	2.90
			5	64.6	1.04
			2.5	36.2	0.45
			1.25	15.8	0.17
17	0.6	44.5	8	98.3	4.12*
			7	97.3	3.63*
			6	96.2	3.28
			5	86.2	1.98
			4	72.4	1.29
			3	41.9	0.54
			2	24.6	0.28
			1	13.3	0.14
18	0.95	17.8	25	83.3	1.79
			12.5	53.6	0.77
			6.25	25.0	0.29
			3.13	13.2	0.14
19	1	16	1.56	4.2	0.04
			12	99.1	
			6	86.2	1.98
			3	45.2	0.60
			1.5	22.0	0.25
			0.75	10.9	0.12
			0.38	3.5	0.04
			0.19	0.9	0.01
20	1	16	0.09	0.8	
			17.5	94.0	2.81
			15	83.5	1.81
			12.5	76.2	1.44
			10	36.0	0.45
			7.5	27.6	0.33
			5	15.7	0.17

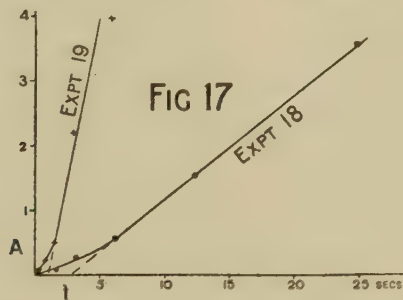
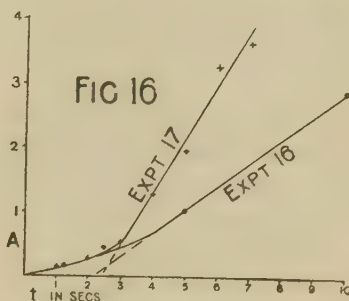
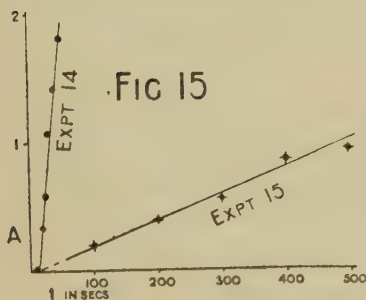
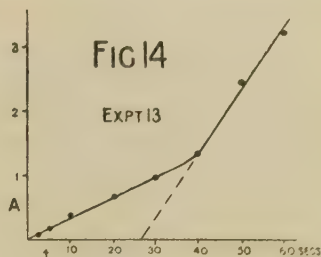
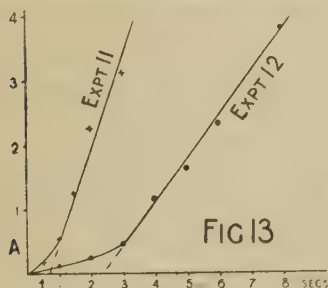
* Doubtful values.

It will be seen from figs. 13-17 that the curve obtained by plotting A against t tends to become a straight line as t becomes great. If A were strictly proportional to t , as it would be upon the Einstein quantum theory of the photo-chemical equivalent, this straight line would pass through the origin, and there would be no initial inhibition period. For the straight line portion, disregarding this inhibition period $A = k_4(t - k_3)$, but what factors k_3 depends upon, it has not yet been possible to discover, though it would appear from the curves that it may be some function of I and t , or it may be a constant for a given condition of grain.

A function of the form

$$[A]_I = k_4(t - k_5[1 - e^{-k_6 t}])$$

where k_6 is not greater than $1/k_5$, will give a curve which represents the



experimental results. A has thus been obtained as a function of I and as a function of t . Hence, since

$$[A]_I = k_1 I (1 - e^{-k_2 I})$$

and

$$[A]_I = k_4 (t - k_5 [1 - e^{-k_6 t}]),$$

therefore

$$A = k_0 I (1 - e^{-k_3 I}) (t - k_5 [1 - e^{-k_6 t}]),$$

where k_0 is a new constant,

or
$$\int_0^t P \cdot dt = \log_e \frac{a}{a-x} = k_0 I (1 - e^{-k_3 I}) (t - k_5 [1 - e^{-k_6 t}]),$$

and this is the equation for the photochemical law of the silver halide grain as deduced from the above experiments.

These results will be applied and extended to the case of the actual photographic plate. The possibility of obtaining this formula for the probability integral on purely theoretical grounds is also under investigation.

Summary.

(1) It has been shown that the silver halide grain is the photochemical unit in the photographic plate.

(2) A method has been devised whereby the law of the photochemical behaviour of these grains can be investigated, free from the disturbing effects of development, etc., which occur in the photographic plate itself.

(3) From experimental results obtained, a formula has been deduced, which shows the relation between the behaviour of the silver halide grains, the light intensity to which they have been exposed, and the time of exposure.

(4) The results show that it is impossible for the mechanism of the process to be the absorption of light in discrete quanta, and that a given amount of light energy has a greater effect photographically when concentrated into a short range of wave-lengths than when it is distributed over a large range.

Dilatation and Compressibility of Liquid Carbonic Acid.

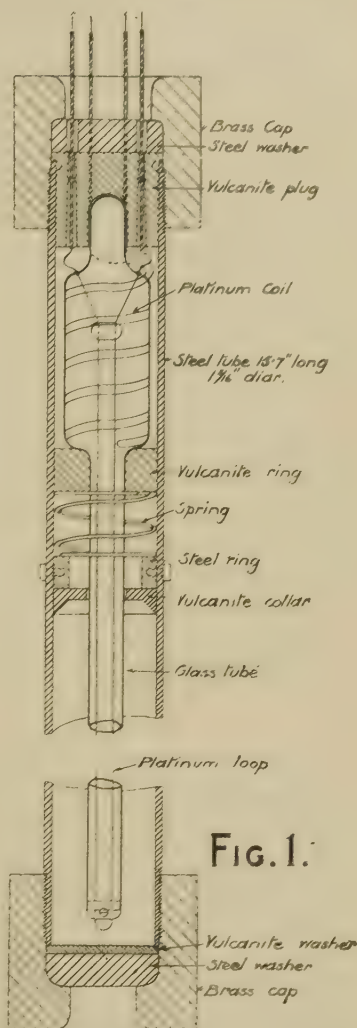
By C. F. JENKIN, C.B.E., M.Inst.C.E., Professor of Engineering Science,
Oxford.

(Communicated by Sir J. Alfred Ewing, K.C.B., F.R.S. Received July 13, 1920.)

In a former paper* it was pointed out that, in order to determine a starting point for drawing the $\theta \phi$, and $I \phi$ diagrams for CO_2 , it was necessary to know the coefficient of expansion of the liquid at constant pressure. The results of a series of measurements on the dilatation and elasticity of the liquid were given (fig. 11, p. 78), but it was pointed out that the results obtained were not in agreement amongst themselves, though sufficiently accurate for the purpose for which they were needed, and it was stated that a new series of measurements were about to be made. These measurements, delayed by the war, have now been completed and are described in the following paper.

* 'Phil. Trans.,' A, vol. 213, p. 76 (1914). The present research was undertaken for the Engineering Committee of the Food Investigation Board of the Department of Scientific Research.

The dilatometer used is shown in fig. 1. It consists of a glass burette, to contain the portion of liquid carbonic acid under examination, enclosed in a steel tube capable of withstanding the necessary pressures. The lower end of the burette dips into mercury, which separates the contents from the rest of the liquid which fills the tube. Round the bulb of the burette a coil of fine platinum wire is wound, which serves as the "bulb" of a platinum thermometer and gives the temperature of the liquid. Inside the burette a long loop of platinum wire is stretched from the top to the bottom; the lower end of this loop is short-circuited by the mercury, so that, by measuring the resistance of the remainder, the height of the mercury in the burette (which cannot be seen inside the steel tube) may be found, and hence the volume of the charge. The connections to these two platinum wires and two additional compensating leads are carried through the vulcanite plug in the top of the steel tube and sealed gas-tight in it by means of small rubber tubes surrounding little brass buttons on the wires, which are drawn tightly into conical holes in the vulcanite. The ends of the steel tube are closed by heavy brass hexagon caps, screwed on, which make gas-tight joints on thin vulcanite washers. The vulcanite plug is supported by a steel washer. The resistances of the two platinum wires are measured with a Callendar and Griffiths bridge, the coils being connected to the bridge alternately by means of a throw-over switch. The one pair of compensating leads serves for both.



When in use the dilatometer stands in the calorimeter shown in fig. 2, which contains a copper coil, forming part of a CO_2 refrigerating circuit, and a number of electrical heaters; by these means the temperature can be maintained at any desired steady value. The calorimeter is filled with

methylated spirits, kept in vigorous circulation by a small electrically-driven centrifugal pump, which draws the spirit down a central tin tube and throws it up round the coils and heaters on the outside. The whole is enclosed in a 2-inch cork jacket, given for the purpose by the Anglo Delta Slab Company, and stands in a wooden box, packed with slag wool.

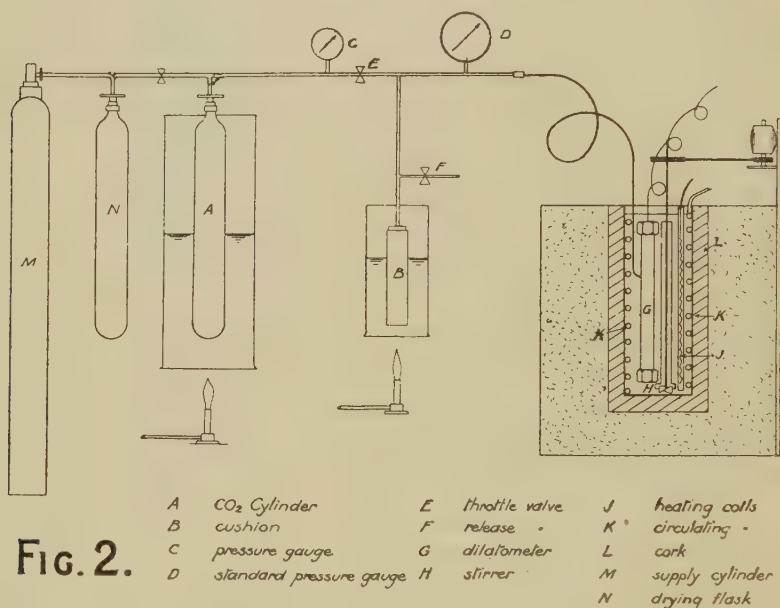


FIG. 2.

The arrangements of the apparatus for charging the dilatometer and regulating the pressure in it when in use are shown in fig. 2 and are used as follows: CO₂ gas is admitted to the whole system from the supply cylinder, M, till the pressure reaches about 10 atmospheres; the cylinder is then shut off and the charge released. This operation is repeated four times to wash out the air. The gas is then admitted up to the full pressure in the supply cylinder, which is warmed till the pressure reaches about 1000 lb./sq. in. At the same time the cylinder, A, is cooled by pouring on cold water and the dilatometer is cooled by wet cloths, and the cushion cylinder is warmed by heating the water in the surrounding vessel. In this way the gas is distilled over and condenses in A and in the dilatometer, but the cushion remains charged with gas: When the apparatus is fully charged the supply cylinder is shut off. Any desired pressure can be applied to the dilatometer by opening the valve E, connecting it to A, which is heated when high pressures are needed, or by closing that connection and releasing gas from the cushion when low pressures are needed. The cushion is used to facilitate the exact regulation of the pressure and is kept hot all the time to prevent liquid condensing in it. The

connection to the dilatometer is made of $\frac{1}{8}$ -inch diameter copper pipe ($\frac{1}{16}$ -inch bore), which is so flexible that the dilatometer can be moved about freely.

Before it is charged the whole of the dilatometer is very thoroughly cleaned. The burette is then put in the steel tube and the top cap screwed on; it is then turned upside down and the burette nearly filled with mercury, and the bottom cap (now on the top) screwed on. It is then gently laid on its side in two crutches, adjusted to hold it nearly level, the bottom end a trifle lower than the top. During this operation the mercury runs out of the burette into the steel tube, but some is left in the side of the bulb; this may be tipped out if desired by again raising and lowering the top end. The mercury is prevented from flowing into the top end of the dilatometer by a vulcanite collar. The dilatometer is charged with liquid CO_2 , as already described, while lying in the crutches. When charged it is raised into the vertical position and the mercury then cuts off the contents of the burette from the rest of the liquid CO_2 outside. The quantity so cut off is, however, more than is wanted and has to be reduced. This is done by heating the dilatometer in the calorimeter beyond the maximum temperature at which any measurements are to be made. During this operation some of the liquid bubbles out through the mercury. The same charge can be retained for more than one day if care is taken to maintain a sufficiently high pressure by keeping the cylinder A above atmospheric temperature or by keeping the dilatometer cooler than the atmosphere in the calorimeter.

Calibrations.

The Callendar and Griffith's bridge was first checked and found to be accurate to the required limits.

The coil of platinum wire wound on the bulb of the burette and used for measuring temperatures was made of a piece of the wire used by the Cambridge Scientific Instrument Company for their platinum thermometers, and is known to have a value of $\delta = 1.5$.* Its length was not adjusted to give a fundamental interval of exactly 1 ohm, but as it turned out to be 1.0041 ohms, the resistances are approximately *platinum temperatures*. To determine the fundamental interval the resistances of the coil were measured in ice, and in the calorimeter at $+30^\circ \text{C}$., as measured by a platinum thermometer. The platinum thermometer was calibrated in ice and steam and also compared with a mercury thermometer which has been calibrated by the N.P.L. The agreements were good, and over the range covered the temperatures are probably accurate to 0.02°C .

* *Vide* Kaye and Laby's 'Physical and Electrical Constants,' p. 46.

The resistances of the loop inside the burette were measured at the same time, and its fundamental interval found. To enable the volume of the enclosed liquid to be deduced from the observed resistance of the platinum loop, a calibration curve connecting volume and resistance was prepared as follows:—A reference line was etched on the burette. Weighed quantities of pure mercury were then poured into the burette, which was fixed vertically upside down, and the difference in level between the meniscus and the reference line measured with a cathetometer. A curve was then drawn connecting volume* and height of meniscus. The burette was then turned right way up and a rubber tube and mercury reservoir connected to it by means of which the mercury was raised step by step in the stem. In each position the resistance of the platinum wire loop was measured by the bridge, and the difference in height between the meniscus and the reference line was read with the cathetometer. A curve was then drawn connecting the resistance and the height of the meniscus. From these two curves the required calibration curve was drawn connecting volume and resistance; it hardly differs perceptibly from a straight line. This curve is only correct for the temperature at which the resistance measurements of the loop were made—hereafter called the standard temperature—and all subsequent resistance measurements of the platinum loop have to be reduced to their corresponding values at standard temperature before the volume can be obtained from the calibration curve; the method of making this reduction is given below.

A small correction has to be made to the observed volumes to allow for the change of volume of the glass burette at different temperatures. Assuming the linear expansion of the soda glass to be 8.5×10^{-6} , the cubical expansion will be $3 \times 8.5 \times 10^{-6}$. As the volume was measured at 13°C. , the correction at -37° amounts to $50^{\circ} \times 3 \times 8.5 \times 10^{-6} = 1.275 \times 10^{-3}$, which is appreciable. The necessary correction has been applied to all the results given in Table I.

Pressures were read on a 10-inch standard gauge calibrated by the N.P.L. It is divided to 10 lb./sq. in. intervals, and pressures can be estimated to 1 lb./sq. in., and are probably correct to 2 lb./sq. in.

Method of Making the Tests.

The dilatometer, having been charged as already described, was put into the calorimeter and the content of the burette reduced to a suitable

* In reducing the weights of the mercury to volume, allowance was made for the buoyancy of the air and the temperature by means of the factors given in Kaye and Laby's 'Phys. and Chem. Constants.'

Table I.—Specific Volumes of Liquid CO₂.

Absolute pressures in lb. per square inch.													
	200.	300.	400.	500.	600.	700.	800.	900.	1000.	1100.	1200.	1300.	1400.
-37° C.	At 162 0·908	0·906	0·904	0·903	0·901	0·900	0·899	0·898	0·896	0·894			
-30° C.	At 206 0·931	0·929	0·927	0·926	0·924	0·922	0·920	0·918	0·916	0·915	0·914		
-20° C.	At 284 0·971	0·970	0·966	0·963	0·961	0·959	0·956	0·954	0·952	0·950	0·948		
-10° C.		At 384 1·025	1·024	1·016 At 505	1·011	1·006	1·002	0·998	0·995	0·993	0·991		
0° C.				1·081 At 580	1·073	1·066	1·060	1·054	1·050	1·045	1·040		
5° C.				1·119	1·116 At 654	1·106	1·098	1·089	1·082	1·076	1·071		
10° C.					1·162 At 740	1·156 At 740	1·144	1·133	1·122	1·113	1·104	1·097	1·090
15° C.						1·221	1·208 At 830	1·190	1·175	1·161	1·150	1·140	1·131
20° C.							1·295	1·272 At 922	1·244	1·222	1·204	1·191	1·179
25° C.								1·395	1·355 [At 1038 1·7]	1·313	1·279	1·254	1·236
30° C.										1·509	1·402	1·343	1·309

amount. The calorimeter was then cooled to zero centigrade, and a series of readings made on the bridge corresponding to a series of pressures from 1200 lb./sq. in. in steps of 100 lb./sq. in. down to a pressure within about 20 lb. of the limit curve. If the limit curve was passed, the liquid in the burette boiled over, and the test had to be started again. At each point the pressure was first adjusted and then final adjustments made to the temperature. Three bridge readings were then taken in rapid succession, viz., resistance of temperature coil, resistance of volume loop, and resistance of temperature coil again. If the temperature had changed more than 0.1° or 0.15° between the first and last readings the results were rejected and another group of readings taken. The pressure was then readjusted to a new value and a fresh set of readings taken, and so on. None of the readings were normally exactly at the desired temperature, and had afterwards to be reduced by a correction depending on the coefficient of thermal expansion of the liquid. As this coefficient is difficult to obtain accurately close to the limit curve, special attention was paid to getting the temperatures accurate for the lowest readings. This was particularly important for the 0° C. series, since the absolute values of all the volumes depended on the assumed specific volume of 0° C. on the limit curve. To make sure of having no temperature correction at this point, a series of consecutive readings were taken alternately of the two resistances while the temperature was allowed to creep very slowly up; this series was continued till the exact zero temperature was just passed. This method might have been adopted for every reading, but was very slow. The temperature could not be raised fast as there was probably an appreciable lag between the temperatures inside and outside the burette.

As soon as the series of readings at zero were completed, the temperature was reduced to -37° C. This was the lowest temperature at which the apparatus could be run without risk of freezing the mercury. After a similar series of readings were taken at that temperature, similar measurements were made at -30° , -20° , -10° , $+5^{\circ}$, $+10^{\circ}$, $+15^{\circ}$, $+20^{\circ}$, $+25^{\circ}$, and $+30^{\circ}$. For the two highest series at $+25^{\circ}$ and $+30^{\circ}$, a smaller charge of liquid had to be used. This was measured by observing its volume at 0° C., near the limit curve, as before.

The observations at low temperatures were smoothly and easily made, but at the high temperatures were more difficult. As it nears the critical point, the liquid becomes both excessively elastic and excessively sensitive to temperature changes—at the critical point, the coefficient of expansion is infinite. One result of this is that, each time the pressure is lowered to adjust it to a new value, the liquid expands, and, in so doing, cools itself,

thus throwing the temperature adjustment out. As the temperature is raised again, the liquid expands, and the pressure has again to be slightly adjusted. For these reasons, getting steady conditions for the observations required much patience, though the conditions were not actually unstable.

Reduction of Results.

Each observation gives three figures:—

- (i) The gauge pressure, P lb./sq. in.
- (ii) The resistance, V , of the platinum loop, which gives the volume of the liquid.
- (iii) The resistance, T , of the platinum coil, which gives the temperature of the liquid.

The true absolute pressure on the liquid is:—

$P \pm$ calibration correction + barometric pressure — difference of height of mercury inside and outside the burette.

The last term is easily obtained sufficiently accurately from the curve already plotted, connecting resistance and height of mercury.

The volume of the liquid was obtained from the resistance, V , as follows:—

Let r_s be the resistance of the whole platinum loop in the burette at the “standard temperature” (*i.e.*, at the temperature of the loop when the calibration curve was prepared).

Let R_s be the resistance of the platinum temperature coil at the same “standard temperature,” let V be the resistance of part of the loop at the temperature of the observation, let T be the resistance of the temperature coil at the same temperature of the observation, let f be the fundamental interval of the loop, F the fundamental interval of the temperature coil, q_s the resistance at the standard temperature of the part of the loop which has the resistance, V , at the temperature of the observation.

Then

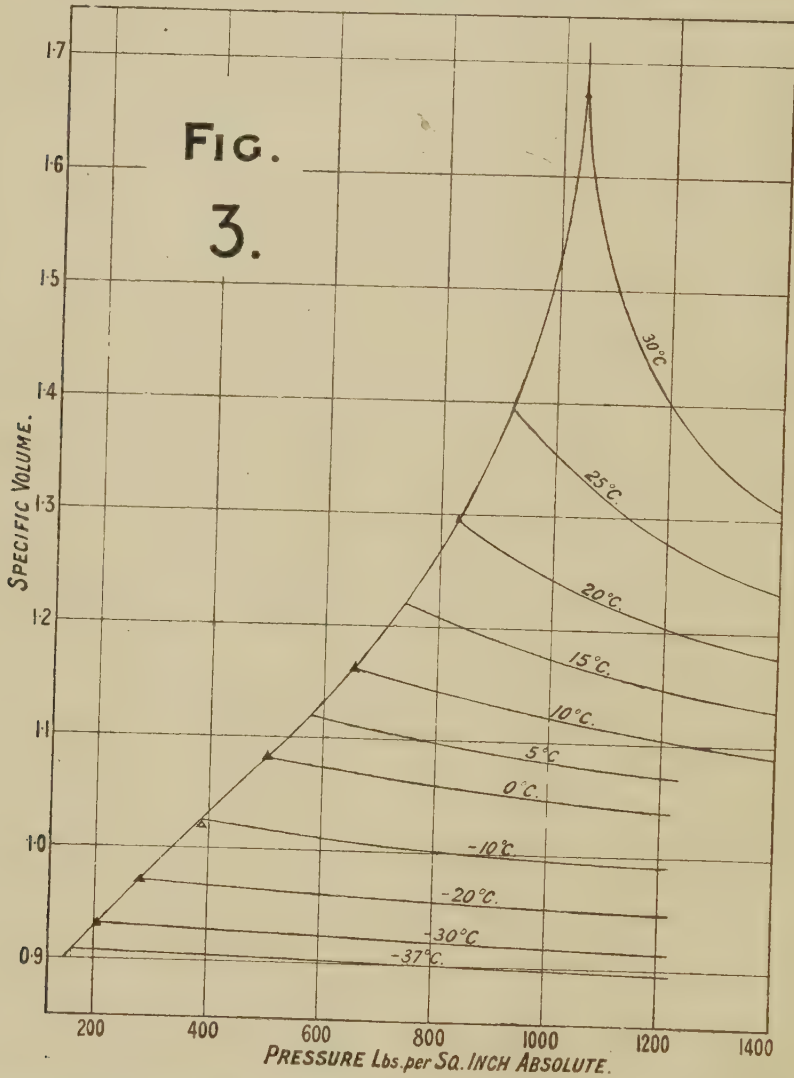
$$q_s = \frac{V r_s}{r_s + f / F (T - R_s)}.$$

The method of finding the values of r_s , R_s , f , and F has already been described under the heading of Calibration. This formula gives q_s , and from q_s the corresponding volume of the liquid was read off the calibration curve.

The exact temperature of the liquid was calculated from the resistance, T (the approximate platinum temperature), in the ordinary way.

The next step was to plot approximate volume/temperature curves for each of the pressures at which readings had been taken, and, from the slopes

of these curves, to calculate approximate temperature coefficients. Using these coefficients, the observed volumes were reduced to values corresponding to the exact temperatures aimed at in making the tests, viz., -37° , -30° , -20° , -10° , 0° , $+5^{\circ}$, $+10^{\circ}$, $+15^{\circ}$, $+20^{\circ}$, $+25^{\circ}$, and $+30^{\circ}$.

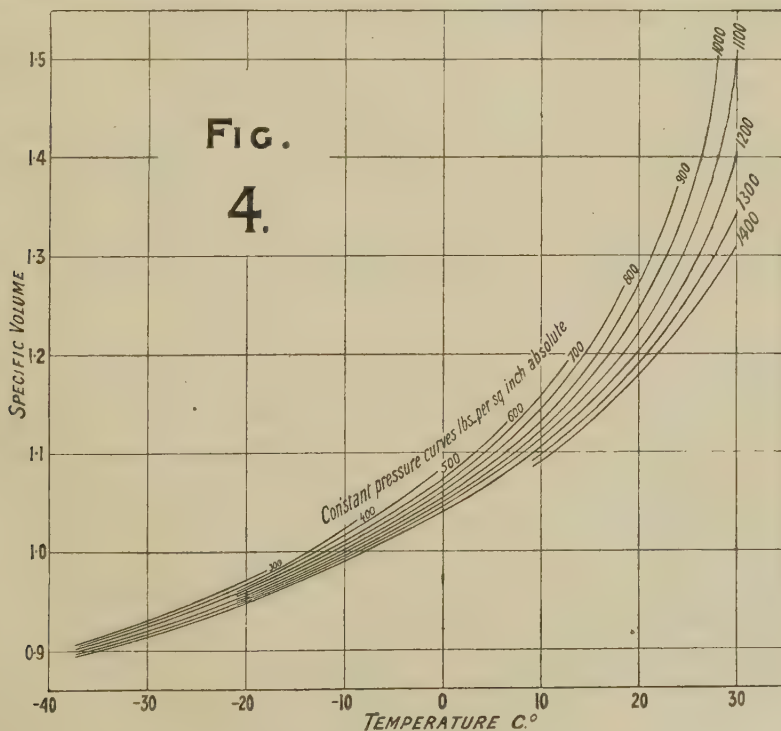


The corrected volumes were then plotted against pressures, each set of observations corresponding to an exact temperature, and smooth curves drawn through the points. The results were found to be remarkably consistent. All the points (except one, which was clearly a misreading) lie very closely indeed on the smooth curves; the average error from the

smooth curve of all the observations (except the one mentioned) is 0.01 c.c., which is the minimum possible reading on the calibration curve, corresponding to 1/10 mm.; it is less than one two-thousandth part of the minimum volume measured; the discrepancies are too small to be shown in the figures reproduced. Observations actually on the limit curve cannot be made by this method, so that the position of the limit curve is fixed entirely on extrapolated curves. At the lower temperatures there can be no appreciable error from this cause, but at 20° there may be a small error, and at 30° the extrapolation is very uncertain.

So far, all the volumes plotted were the actual volumes of the liquid CO₂ in the burette; they had now to be reduced to specific volumes. For this purpose, the specific volume of the liquid on the limit curve at 0° C. was assumed to be at 1.081, *i.e.*, the value found by Behn.* The observed volumes were therefore reduced in the ratio of the observed volume at 0° C. on the limit curve to Behn's specific volume and re-plotted; the resulting curves are shown in fig. 3.

From these curves, the specific volumes at each even hundred pounds pressure were plotted against temperatures; the results are shown in fig. 4.



* 'Annalen der Physik,' Ser. IV, vol. 3, p. 733 (1900).

The results are tabulated in Table I, after applying the very small correction due to the temperature coefficient of the glass burette.

The slopes of each set of curves were then measured and the true compressibilities, $\frac{1}{v} \left\{ \frac{dv}{dp} \right\}_t$ and temperature coefficients $\frac{1}{v} \left\{ \frac{dv}{dt} \right\}_p$ were calculated; the results are given in Tables II and III. These values are only given to two (or sometimes three) significant figures; very slight alterations in the curves produce large changes in their slopes, and no great accuracy can be claimed for the tabulated figures (Tables II and III).

Errors.

The method of measuring the elasticity and dilatation is simple and direct, and does not appear to be liable to any serious errors. The following errors have been considered.

The mercury meniscus is concave towards the bulb while the volume calibration is made, but convex towards the bulb when it contains CO_2 . The actual content of the burette is therefore larger than the assumed value by twice the volume between the meniscus and a tangent plane on the top of it. The height of the meniscus in air was found to be about $\frac{3}{4}$ mm., and an outside estimate of this error shows that it is negligible.

The compression of the glass burette due to the difference between the internal and external pressures is negligible. The compression of the glass due to the maximum pressure on it (1400 lb./sq. in.) produces negligible errors in the reading of the burette. Friction of the mercury in the burette was entirely eliminated by a slight constant vibration due to want of balance of the circulating pump propeller.

Impurities in the CO_2 —Air.—In one of the early trials a serious difficulty occurred. As the pressure was reduced, normal expansion of the liquid in the burette took place till the pressure was about 150 or 100 lb./sq. in. above the limiting pressure, when suddenly the liquid began to expand rapidly, and the burette “boiled over.” The cause of this boiling over was traced to the presence of air dissolved in the liquid CO_2 ; analysis showed that the gas contained 1.6 per cent. by volume of air, whereas the normal gas supply only contained 0.11 per cent. On a later occasion the same trouble occurred when the gas was found to have 3.4 per cent. of air in it. The whole stock of gas (five cylinders) in hand at that time was then analysed and found to contain abnormally high percentages of air. After various trials it was found possible to obtain air-free CO_2 by blowing off a considerable amount of gas from the top of the supply cylinder and then

Table II.—Compressibility of Liquid CO₂. True Coefficient of Compressibility $1/v (dv/dp)_t$.

Absolute pressure lb./sq. in.	-37° C.	-30° C.	-20° C.	-10° C.	0° C.	5° C.	10° C.	15° C.	20° C.	25° C.	30° C.
200	1.5×10^{-5}	2.1×10^{-5} (at 210)	3.8×10^{-5} (at 300)	6.2×10^{-5}	7.25×10^{-5} (at 520)	9.7×10^{-5}	11.9×10^{-5} (at 650)	16.3×10^{-5} (at 820)	28×10^{-5} (at 920)	41×10^{-5} (at 920)	114×10^{-5} at 1100 51×10^{-5} at 1200 34×10^{-5} at 1300 19×10^{-5} at 1400
400	—	2.0×10^{-5}	3.4×10^{-5}								
600	—	1.9×10^{-5}	2.8×10^{-5}	4.7×10^{-5}	4.5×10^{-5}	6.2×10^{-5}	8.2×10^{-5}	12.0×10^{-5}	20×10^{-5}		
800	—	1.8×10^{-5}	2.4×10^{-5}	3.6×10^{-5}	4.5×10^{-5}	6.2×10^{-5}	8.2×10^{-5}	12.0×10^{-5}	20×10^{-5}		
1000	—	1.7×10^{-5}	2.0×10^{-5}	2.8×10^{-5}	4.5×10^{-5}	6.2×10^{-5}	8.2×10^{-5}	12.0×10^{-5}	20×10^{-5}		
1200	—	1.6×10^{-5}	1.8×10^{-5}	2.2×10^{-5}	3.7×10^{-5}	5.0×10^{-5}	6.5×10^{-5}	8.8×10^{-5}	13.3×10^{-5}		
1400	—	1.5×10^{-5}	1.6×10^{-5}	2.0×10^{-5}	3.0×10^{-5}	3.9×10^{-5}	5.0×10^{-5}	6.3×10^{-5}	8.3×10^{-5}		

The coefficients are expressed per lb./sq. inch. To obtain the coefficients per atmosphere, multiply by 14.7. To obtain the coefficients per megabar, multiply by 14.5.

Table III.—Dilatation of Liquid CO₂. True Coefficient of Expansion $1/v (dv/dt)_p$.

Absolute pressure lb./sq. in.	-37° C.	-30° C.	-20° C.	-10° C.	0° C.	5° C.	10° C.	15° C.	20° C.	25° C.	30° C.
300	3.3×10^{-3}	3.8×10^{-3}	5.1×10^{-3}	6.3×10^{-3}	$(\text{At } -1^\circ \text{ C.})$ 7.4×10^{-3}	8.4×10^{-3}	10.0×10^{-3}	12.5×10^{-3}	15.5×10^{-3}	18.0×10^{-3}	21.7×10^{-3}
400	3.2×10^{-3}	3.7×10^{-3}	4.7×10^{-3}								
500	3.1×10^{-3}	3.6×10^{-3}	4.5×10^{-3}	5.7×10^{-3}	7.0×10^{-3}	7.8×10^{-3}	9.2×10^{-3}	11.2×10^{-3}	13.1×10^{-3}	15.5×10^{-3}	18.0×10^{-3}
600	3.0×10^{-3}	3.5×10^{-3}	4.4×10^{-3}	5.4×10^{-3}	6.6×10^{-3}	7.4×10^{-3}	8.5×10^{-3}	10.0×10^{-3}	11.5×10^{-3}	13.1×10^{-3}	15.4×10^{-3}
700	3.0×10^{-3}	3.4×10^{-3}	4.3×10^{-3}	5.2×10^{-3}	6.3×10^{-3}	7.0×10^{-3}	7.9×10^{-3}	9.0×10^{-3}	10.4×10^{-3}	11.6×10^{-3}	13.9×10^{-3}
800	3.0×10^{-3}	3.4×10^{-3}	4.2×10^{-3}	5.0×10^{-3}	6.0×10^{-3}	6.7×10^{-3}	7.4×10^{-3}	8.3×10^{-3}	9.6×10^{-3}	10.6×10^{-3}	12.9×10^{-3}
900	2.9×10^{-3}	3.3×10^{-3}	4.1×10^{-3}	4.8×10^{-3}	5.7×10^{-3}	6.3×10^{-3}	7.0×10^{-3}	7.7×10^{-3}	8.8×10^{-3}	9.1×10^{-3}	10.6×10^{-3}
1000	2.8×10^{-3}	3.2×10^{-3}	4.0×10^{-3}	4.7×10^{-3}	5.5×10^{-3}	6.1×10^{-3}	6.8×10^{-3}	7.4×10^{-3}	8.4×10^{-3}	8.6×10^{-3}	10.0×10^{-3}
1100	2.8×10^{-3}	3.2×10^{-3}	3.9×10^{-3}	4.6×10^{-3}	5.4×10^{-3}	5.9×10^{-3}	6.6×10^{-3}	7.2×10^{-3}	8.0×10^{-3}	8.6×10^{-3}	10.0×10^{-3}
1200	2.7×10^{-3}	3.1×10^{-3}	3.8×10^{-3}	4.5×10^{-3}	—	—	—	—	—	—	—
1300	—	—	—	—	—	—	—	—	—	—	—
1400	—	—	—	—	—	—	—	—	—	—	—

The coefficients are expressed per degree centigrade. To obtain the coefficients per degree Fahrenheit, multiply by 5/9.

inverting it and drawing off liquid CO_2 for use, from the bottom. Analysis of gas obtained in this manner showed that there was not more than 0.01 per cent. of air present.

Water.—Experience has shown that drying flasks or tubes of calcium chloride do not completely dry the gas. Ice always collects at points of low temperature, however carefully the gas has been dried. An arithmetical error in reducing the results of the tests at the higher temperatures made them appear to fall decidedly above Behn's results, and a possible explanation appears to be the presence of water dissolved in the liquid. A special series of measurements was therefore made on a specially prepared sample of CO_2 which was freed as far as possible from water by cooling it below zero centigrade.

The following method of freezing out the water was adopted:—The burette was filled with mercury and enclosed in the steel tube, and the whole charged with liquid CO_2 in the usual manner, but before inverting the apparatus it was cooled to -10°C . by spraying the tube externally with ethyl chloride, and kept at about that temperature for half an hour. It may be supposed that any water would freeze out during this operation and be deposited as ice inside the steel tube. To prevent any ice forming where the mercury might subsequently wash it off, a paper lining was put inside the steel tube extending about 3 inches from the bottom. After half an hour's freezing in this way the apparatus was inverted as usual so that the burette filled with the dried CO_2 . The mercury was sealed off the charge and the tube could be warmed without any fear of water entering the burette.

The measurements made on this dried sample showed that the specific volumes were very slightly lower than those of the earlier samples, which probably contained traces of moisture. After these results had been obtained the arithmetical error mentioned above was discovered, and explained the much larger discrepancies which these tests had been made to elucidate.

The curves and figures given for temperatures above zero refer to the specially dried sample. For all temperatures below zero the water must have frozen out, so that they too refer to dried samples. The difference between the dried and wet samples above zero are quite small. No information can be obtained from these small differences, because the amounts of water and air present in the actual samples tested cannot be determined.

Radiation in Explosions of Hydrogen and Air.

By W. T. DAVID, M.A., D.Sc.

(Communicated by Prof. H. L. Callendar, F.R.S. Received May 13, 1920).

In the first part of this paper the results of experiments are recorded on the emission of radiation during explosion and subsequent cooling of inflammable mixtures of hydrogen and air contained in a closed vessel; and in the second part of the paper some experiments bearing on the transparency of the hot gaseous mixtures after explosion are described.

The results of a similar investigation in connection with inflammable mixtures of coal-gas and air have already been published.* The laws governing the emission of radiation in the hydrogen mixtures would appear to be similar in many ways to those governing the emission in the coal-gas mixtures; but in one or two respects there are important differences, which are of considerable interest in their bearing upon gaseous combustion.

Method of Experiment.

Full details of the experimental methods and apparatus employed have been given in the paper recording the results of the coal-gas and air experiments, but it will be convenient to describe them here very briefly. The inflammable mixtures were exploded in a cylindrical cast-iron vessel, 30 cm. in diameter and 30 cm. in length (see fig. 1). The pressure of the gaseous mixtures during explosion and subsequent cooling was measured by means of a Hopkinson optical indicator, which threw a spot of light on to a revolving photographic film. The radiation was measured by means of a platinum bolometer connected with a reflecting galvanometer, which also threw a spot of light on to the same revolving film. The bolometer was protected from the hot gaseous mixtures by means of a plate of fluorite, as shown in fig. 1. The fluorite transmits almost exactly 95 per cent. of radiation of the wave-length emitted by exploded hydrogen and air mixtures. After making an allowance of 5 per cent. for the absorption of the fluorite and 5 per cent. for reflection from the blackened surface of the bolometer, it is considered that the measurements from the films give radiation values of a high degree of accuracy.

The radiation emitted was measured in three positions on one of the end-covers of the explosion vessel, viz., at the top (position A, fig. 1), at the bottom (position B), and at the centre (position C).

* 'Phil. Trans.,' A, vol. 211, pp. 375-410.

When the bolometer was placed close up to the fluorite window, the radiation it received per square centimetre of its surface was equal to that received by a square centimetre of wall surface in the immediate neighbourhood; and when the bolometer was placed some distance away from the fluorite windows, the radiation it received came from a cone of the gaseous mixture of small solid angle (N , as shown in fig. 1). The experiments described in the first part of the paper were all made with the bolometer placed close to the fluorite window. Those described in the second part of the paper were made with the bolometer placed some distance behind the window. The measurements with the bolometer in this latter position have been divided

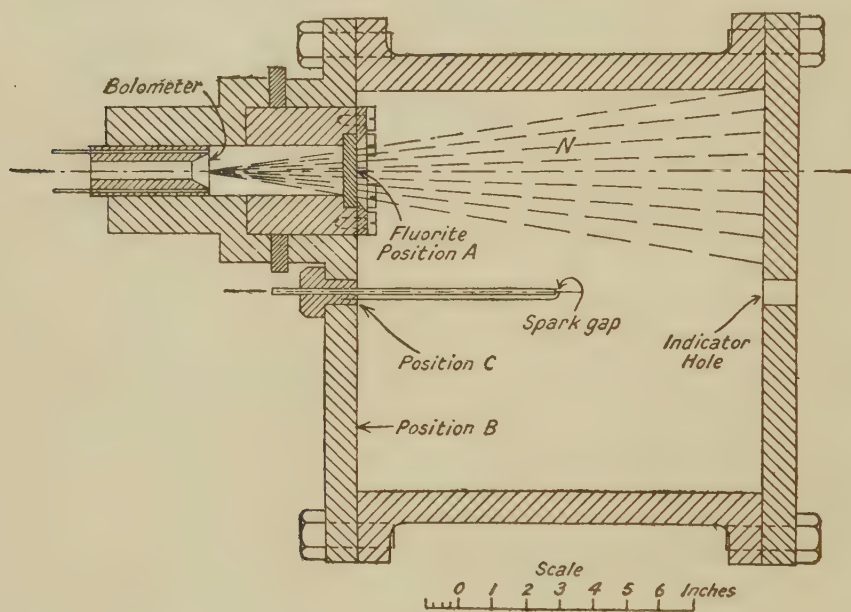


FIG. 1.

by the solid angle of the cone, so as to give the radiation from a cone of unit solid angle; and, following Prof. Callendar, this has been called the *intrinsic radiance*.

The hydrogen used in these experiments was supplied by the British Oxygen Company, guaranteed 98 per cent. pure.

PART I.—TOTAL RADIATION MEASUREMENTS.

Hydrogen and Air Mixtures of various Strengths.

The curves in fig. 2 relate to 25.4 per cent., 15.3 per cent., and 10.0 per cent. mixtures of hydrogen and air. Curves A_T , B_T , and C_T are the mean gas

temperature curves for these mixtures respectively. These have been calculated from the pressure records by means of the equation $pv = R\theta$, after making an allowance for the large contraction of volume which occurs during combustion. The radiation curves for the various mixtures, A_R , B_R , and C_R are the means of those measured in positions A, B, and C (see fig. 1),* and give, it is thought, a fairly reliable estimate of the mean radiation over the whole of the vessel walls. The dotted curve A'_R , B'_R , and C'_R are the differentials of the mean radiation curves and give the mean rate at which the walls of the vessel receive radiation per square centimetre per second at various times after ignition.

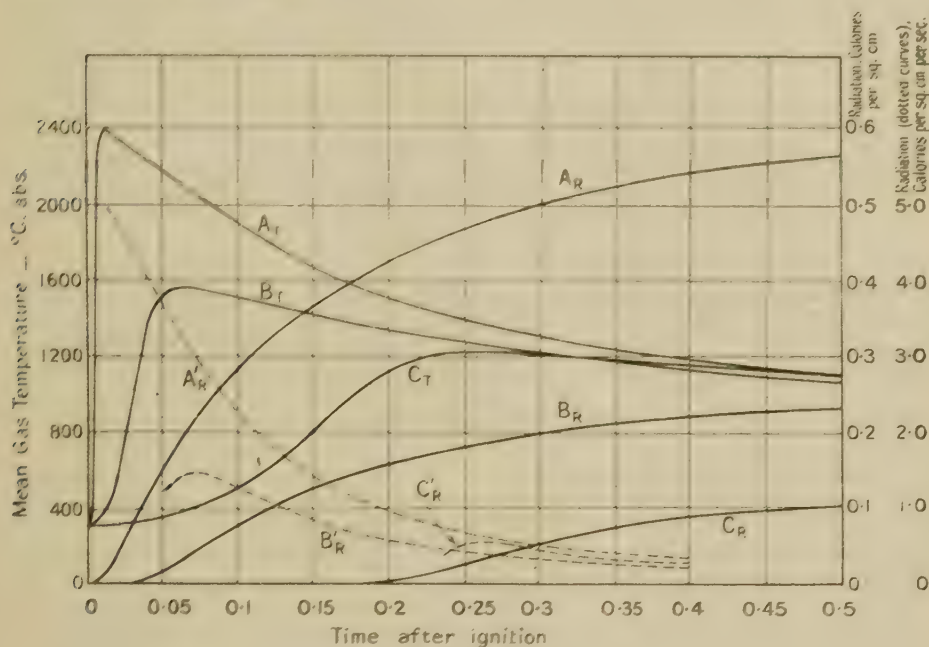


FIG. 2.

Tables I, II, and III have been prepared from the gas temperature and radiation curves in this figure. They show the mean radiation received by

* The rate at which radiation is received by the walls is from 10 to 20 per cent. greater in position C than in the other positions. The radiation curve for the 10 per cent. mixture has been calculated from a film record giving the emission from a cone of small solid angle of the gaseous mixture, which is proportional to the total radiation measured when the bolometer is placed close up to the plate of fluorite. This curve may not compare as regards accuracy with the curves for other mixture strengths both for this reason, and also because one record only was taken; but it is, I believe, substantially correct. All the experiments in the first part of this paper were made with the walls of the explosion vessel covered with a thin layer of dull black paint, so as to absorb all the radiation falling upon them.

Table I.—25·4 per cent. Mixture of Hydrogen and Air. Initial Pressure, Atmospheric. Heat of Combustion of Hydrogen in Vessel = 16,320 calories.

Time from ignition (secs.).	Mean absolute temperature of gaseous mixture (° C. abs.).	Mean radiation received by walls per sq. cm. (calories).	Total loss of heat by radiation per cent. heat of combustion.
0·017	2400 (max. temp.)	0·018	0·5
0·05	2200	0·15	4·0
0·1	1920	0·285	7·7
0·15	1700	0·37	10·0
0·2	1530	0·425	11·4
0·25	1400	0·47	12·6
0·5	1100	0·57	15·5
0·75	910	0·59	15·8
1·0	810	0·60	16·1

Table II.—15·3 per cent. Mixture of Hydrogen and Air. Initial Pressure, Atmospheric. Heat of Combustion of Hydrogen in Vessel = 9700 calories:

Time from ignition (secs.).	Mean absolute temperature of gaseous mixture (° C. abs.).	Mean radiation received by walls per sq. cm. (calories).	Total loss of heat by radiation per cent. heat of combustion.
0·065	1580 (max. temp.)	0·03	1·3
0·1	1510	0·085	3·8
0·15	1410	0·13	5·9
0·2	1340	0·16	7·2
0·25	1280	0·18	8·2
0·5	1080	0·23	10·3
0·75	900	0·24	10·8
1·0	810	0·245	11·0

Table III.—10·0 per cent. Mixture of Hydrogen and Air. Initial Pressure, Atmospheric. Heat of Combustion of Hydrogen in Vessel = 6450 calories.

Time from ignition (secs.).	Mean absolute temperature of gaseous mixture (° C. abs.).	Mean radiation received by walls per sq. cm. (calories).	Total loss of heat by radiation per cent. heat of combustion.
0·24	1230 (max. temp.)	0·02	1·4
0·25	1220	0·03	2·0
0·3	1200	0·055	3·7
0·35	1180	0·075	5·1
0·4	1150	0·085	5·7
0·45	1120	0·095	6·4
0·5	1100	0·105	7·1
1·0	850	0·12	8·2

the walls per square centimetre and the proportion of the heat of combustion lost by radiation at various times after ignition. Table IV, which has been compiled from these tables, shows the total radiation received by the walls per square centimetre and the proportion of the heat of combustion lost by radiation during explosion and subsequent cooling in the various mixtures. Similar information in regard to coal-gas mixtures has been added for purposes of comparison.

It will be seen from the figures in Table IV that the proportion of the heat of combustion radiated off during explosion and subsequent cooling in the hydrogen mixtures varies greatly with the mixture strength, whereas in the coal-gas mixtures the variation in this proportion is small. Experiments on the analysis of the radiation emitted, which will be described presently, offer an explanation of these results.

It has been shown* that the total radiation emitted in coal-gas mixtures in the experimental vessel is a linear function of the maximum temperature developed. This relation is expressed by the equation

$$R_T = 0.00056 (\theta_{\max.} - 700),$$

where R_T is the total radiation received by the walls per square centimetre of surface, and $\theta_{\max.}$ is the maximum absolute temperature developed. A similar relation for the hydrogen mixture, based upon the three sets of figures in Table IV, is

$$R_T = 0.00042 (\theta_{\max.} - 950).$$

This equation, it is believed, may be relied upon to give reliable values of R_T for all hydrogen and air mixtures, at atmospheric density, within the limits of mixture strength 10 per cent. to 25 per cent., when exploded in a cylindrical vessel 30 cm. in diameter and 30 cm. in length, whose walls are blackened.

Table V has also been compiled from the figures in Tables I, II, and III. It shows the proportion of the heat of combustion lost by radiation up to the moment of maximum pressure in the hydrogen mixtures. Figures relating to coal-gas mixtures have been added for purposes of comparison.

It will be seen that, in the case of the coal-gas mixtures, the proportion of the heat of combustion radiated off during the explosion period increases very considerably as the mixture strength becomes weaker—a result which must be explained in terms of the increasing time of explosion, for the temperatures developed are, of course, lower in the weaker mixtures. In the case of the hydrogen mixtures, however, the increase in this proportion, as the mixture strength decreases, is not marked, even though in the weakest

* 'Phil. Mag.,' January, p. 81 (1920).

Table IV.

Hydrogen Mixtures.				Coal-gas Mixtures.			
Percentage strength of mixture.	Maximum temperature developed ($\theta_{\max}$).	Total radiation received by walls per sq. cm. (R_T).	Total loss of heat by radiation per cent. heat of combustion.	Percentage strength of mixture.	Maximum temperature developed. ($\theta_{\max}$).	Total radiation received by walls per sq. cm. (R_T).	Total loss of heat by radiation per cent. heat of combustion.
25.4	2400	0.60	16.1	15.0	2410	0.98	26.1
15.3	1580	0.245	11.0	13.0	2170	0.81	25.0
10.0	1230	0.12	8.2	9.8	1700	0.57	23.6

Table V.

Hydrogen Mixtures.				Coal-gas Mixtures.			
Percentage strength of mixture.	Time of explosion (secs.).	Maximum temperature developed ($^{\circ}$ C. abs.).	Percentage heat of combustion lost by radiation up to maximum pressure.	Percentage strength of mixture.	Time of explosion (secs.).	Maximum temperature developed. ($^{\circ}$ C. abs.).	Percentage heat of combustion lost by radiation up to maximum pressure.
25.4	0.017	2400	0.5	15.0	0.05	2410	3.3
15.3	0.065	1580	1.3	13.0	0.07	2170	3.7
10.0	0.24	1230	1.4	9.8	0.18	1700	7.0

mixture the time of explosion is as much as 0.24 second. The difference in the behaviour of the hydrogen and the coal-gas mixtures in this respect is interesting, and will be discussed presently in connection with later experiments.

The curves in fig. 3 have been prepared from the dotted curves in fig. 2. They show the rate at which the walls receive radiation per square centimetre per second during the cooling of the various hydrogen mixtures after explosion. The figures in Table VI have been compiled from the curves in

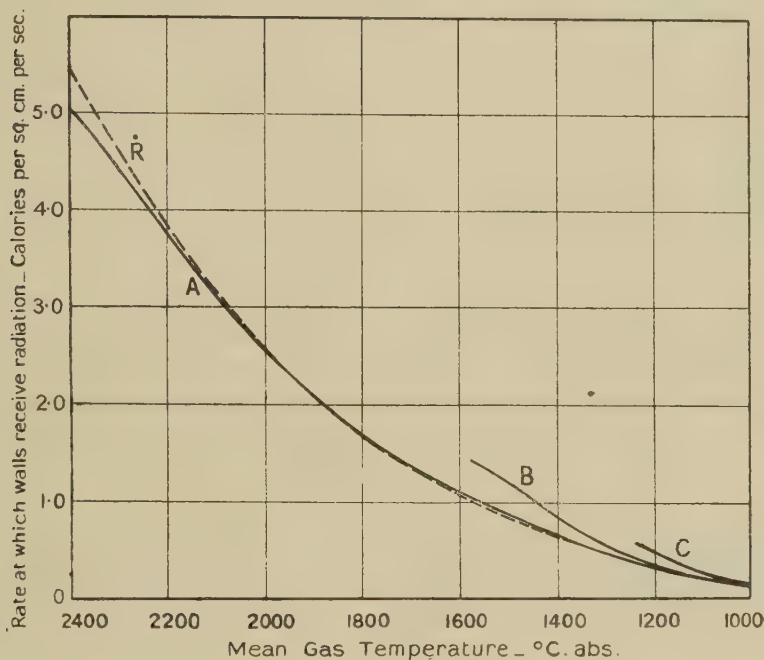


FIG. 3.

Curve A.—25.4 per cent. mixture of hydrogen and air.

„ B.—15.3 „ „ „

„ C.—10.0 „ „ „

„ $\dot{R} = 1.65 \times 10^{-14} \theta^4$.

this figure, and similar information has been added for coal-gas mixtures. This table shows that the hydrogen mixtures emit radiation at approximately the same rate as the coal-gas mixtures. They also show that the weak hydrogen mixtures, like the weak coal-gas mixtures, radiate more powerfully in the initial stages of cooling than the strong mixtures when they have cooled to the temperatures which the weak mixtures have in this epoch.

Table VI.

Mean gas temperature (° C. abs.).	Rate at which walls of vessel receive radiation, calories per sq. cm. per sec.					
	Hydrogen Mixtures.			Coal-gas Mixtures.		
	25·4 per cent.	15·3 per cent.	10·0 per cent.	15·0 per cent.	13·0 per cent.	9·8 per cent.
2400	5·0	—	—	5·4	—	—
2200	3·8	—	—	3·9	—	—
2170	—	—	—	3·7	4·0	—
2000	2·55	—	—	2·7	2·9	—
1800	1·7	—	—	1·8	1·8	—
1700	—	—	—	1·45	1·45	1·8
1600	1·1	—	—	1·15	1·15	1·2
1580	1·08	1·45	—	—	—	—
1400	0·7	0·85	—	0·65	0·65	0·65
1230	0·4	0·4	0·6	—	—	—
1200	0·35	0·35	0·5	0·3	0·3	0·3
1000	0·15	0·15	0·2	0·15	0·15	0·15

It has been shown* that the rate at which the walls receive radiation per square centimetre per second ($\dot{R}$) may, in the case of the coal-gas and air mixtures at atmospheric density, be estimated approximately by means of the equation

$$\dot{R} = 1.75 \times 10^{-14} \theta^4,$$

where $\dot{R}$ is expressed in calories per square centimetre per second and θ in degrees C. absolute. A very similar equation answers approximately in the case of the strong hydrogen mixtures. The equation to the dotted curve in fig. 3 is

$$\dot{R} = 1.65 \times 10^{-14} \theta^4.$$

Perhaps the most noticeable difference between radiation phenomena in hydrogen mixtures and those in coal-gas mixtures, as revealed by these experiments, is that, in the latter mixtures, the maximum rate at which radiation is emitted occurs during the explosion period,† when chemical activity is proceeding with great violence, while, in the hydrogen mixtures, it occurs at the moment of attainment of maximum temperature (or, indeed, perhaps a little later), when chemical activity has presumably in a large measure ceased. This is clearly shown by the dotted curves B_R' and C_R' (fig. 2),

* 'Phil. Mag.,' January, p. 79 (1920).

† The maximum rate of emission in the coal-gas mixture occurs near the time when the pressure curves undergo their second inflexion. See 'Phil. Mag.,' January, p. 70 (1920), and 'Phil. Trans.,' A, vol. 211, p. 381.

which give the rates of emission of radiation in the 15·3 per cent. and the 10·0 per cent. hydrogen mixtures respectively.

A quite different result was obtained in the case of the coal-gas mixtures when the bolometer was protected by windows of quartz and plate glass, which transmit for the most part radiation from steam, and cut off the bulk of that emitted by carbon dioxide. Records taken in this way show that the maximum rate of emission occurs near the second point of inflexion of the gas temperature curve during the explosion period—that is, at the same point as records taken with a fluorite window (which transmits radiation from both carbon dioxide and steam), show their maximum value.

Analysis of the Radiation Emitted in Hydrogen and Air Mixtures.

The infra-red spectrum of a hydrogen flame consists mainly of a well defined band, whose maximum is approximately at $2\cdot8\mu$, and there is little doubt that this band would be prominent in the spectrum of an exploded hydrogen mixture, though it may be somewhat broader than that of the naked flame, owing to the exploded mixture being at a higher pressure.* Radiation of other wave-lengths, however, would appear to be emitted in exploded hydrogen mixtures, as will be seen from the following experiments.

Table VII has been prepared from experiments made on 25·4 per cent. mixtures, first, when the bolometer was protected by the fluorite plate, and, secondly, when the fluorite plate was replaced by a plate of quartz.

Table VII.—Rate at which Radiation is received from 25·4 per cent. Mixtures of Hydrogen and Air per sq. cm. per sec. through Plates of Fluorite and Quartz. Bolometer in Position A.

Time from ignition (secs.).	Mean gas temperature. (° C. abs.).	Fluorite.	Quartz.	$\frac{\text{Quartz}}{\text{Fluorite}}$
0·017	2400	4·7	3·65	0·79
0·045	2200	3·5	2·6	0·74
0·07	2000	2·45	1·65	0·67
0·12	1800	1·7	1·0	0·59
0·175	1600	1·1	0·6	0·55
0·25	1400	0·7	0·3	0·43
0·38	1200	0·35	0·1	0·29
0·60	1000	0·15	Nearly zero	Nearly zero

The quartz plate transmits about 70 per cent. of the radiation of wave-lengths between 2μ and $3\cdot5\mu$. It is more transparent than this to radiation

* Schaefer ('Ann. der Phys.,' vol. 16, I., p. 93) found that the *absorption bands* of CO_2 broadened as the pressure of the absorbing gas was increased.

of shorter wave-length than 2μ , and is opaque to radiation of greater wave-length than 3.5μ . The fluorite plate transmits almost exactly 95 per cent. of radiation over a very wide range of the infra-red spectrum (down to about 11μ). The radiation measurements through the fluorite plate have been corrected to the extent of 5 per cent. for this absorption, and if the emission spectrum of the hydrogen mixtures consisted simply of the 2.8μ band throughout cooling, it would have been expected that the ratio of the rate of emission through quartz to that through fluorite would have been fairly constant at about 0.7 for all gas temperatures.

This, however, was not found to be the case, as may be seen from Table VII. The ratio of the emission through quartz to that through fluorite decreases as the temperature decreases, indicating that there must be emitted by this mixture some radiation of greater wave-length than 3.5μ , which becomes of increasing importance relatively to the 2.8μ radiation as the temperature decreases.

At 1200° C. abs. the ratio is only 0.29, and at 1000° C. abs. it is practically zero. From these figures, it must be inferred that, in the neighbourhood of 1200° C. abs., the 2.8μ radiation is rapidly ceasing to be emitted, and that, when the gas temperature has fallen to 1000° C. abs., it has practically ceased, whereas, at these temperatures, radiation of greater wave-length continues to be emitted in appreciable quantities.

In the neighbourhood of the maximum temperature (2400° C. abs. to 2200° C. abs.), the ratio of the emission through quartz to that through fluorite is a little greater than 0.7. After making an allowance of 30 per cent. for the absorption of quartz, the radiation registered through quartz would thus appear to be greater than that registered through fluorite. A probable explanation of this is that in this epoch there is considerable energy in radiation of shorter wave-length than 2.8μ , for which the absorption of the quartz plate is much less than 30 per cent.*

* At first sight the explanation of these results might appear to lie in a possible shifting of the " 2.8μ band" towards the shorter wave-length with rise of temperature and towards the greater wave-lengths as the temperature decreases. Such an explanation, however, would involve a shifting to an extent which is scarcely probable—from say about 1μ at 2400° C. abs. to about 4μ at 1000° C. abs. Some interesting possible explanations may be inferred from the following facts discovered by Coblenz:—(i) The absorption spectrum of water vapour shows a strong band (or series of bands) extending from about 4μ to about 8μ ; (ii) the absorption spectrum of oxygen (of which there is a little in the exploded mixtures) shows shallow bands whose maxima are at 3.2μ and 4.7μ ; and (iii) nitrogen (of which there is, of course, a large amount in the exploded mixtures) gives a strong emission band in a vacuum tube whose maximum is at 1μ approximately.

PART II.—INTRINSIC RADIANCE AND TRANSPARENCY MEASUREMENTS.

The curves in fig. 4 show the rate of emission of radiation from unit solid angle (*i.e.*, the intrinsic radiance) of 25·4 per cent. hydrogen mixtures at various gas temperatures. Curve A gives the intrinsic radiance of the

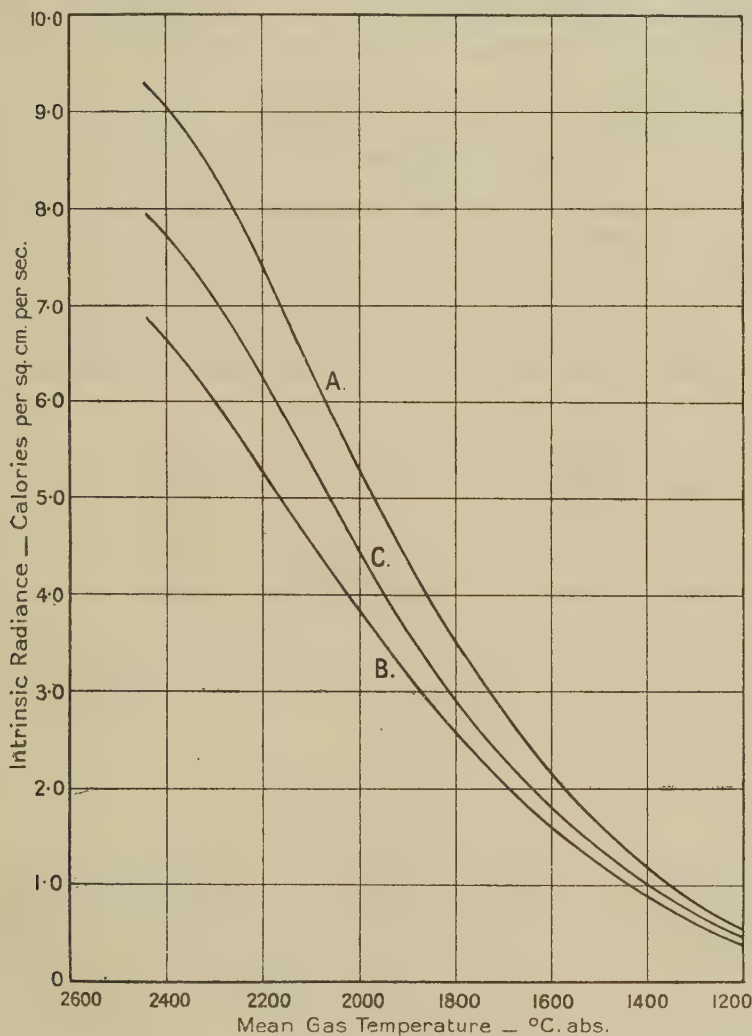


FIG. 4.

mixture when contained in the vessel with its silver-plated walls polished. Curve B gives the intrinsic radiance of the mixture when the walls of the vessel were blackened; and curve C gives similar information in respect to a mixture of the same composition contained in the blackened vessel with a polished circular patch (about 6 inches in diameter) on the end-cover opposite

the bolometer. By this means the cone of gas from which the radiation is measured is reflected back upon itself and its virtual length is thus 60 cm. (*i.e.*, double the length of the vessel), or rather from a virtual thickness of 59 cm. allowing from 2 to 3 per cent. for the absorption of the silver-plating.

From curves A and B (fig. 4) it will be seen that the hydrogen mixture in the polished vessel emits about 35 per cent. more strongly than in the blackened vessel—the emission being compared in the two cases at the same mean gas temperature. Coal-gas mixtures under similar conditions emitted about 65 per cent. more strongly in the polished vessel than in the black vessel in the initial stages of cooling and about 50 per cent. more strongly after the gas temperature had fallen to about 1600° C. abs.* When discussing the coal-gas results it was pointed out that they were probably due to the vibratory energy of the radiating molecules and the transparency of the gaseous mixture being greater in the polished vessel than in the black vessel, and it is probable that similar causes are responsible for the hydrogen results.

An indication of the transparency of the hydrogen mixtures in the black vessel to radiation of the same kind as they emit may be obtained by comparing the intrinsic radiance from 59 cm. (curve C) with that from 30 cm. (curve B). This comparison is made in Table VIII and a similar comparison for coal-gas mixtures is added. It will be seen that the intrinsic radiance from 59 cm. is about 15 per cent. greater than that from 30 cm. in the early stages of cooling and drops to about 10 per cent. after the gas temperature has fallen to about 1600° C. abs. The ratios for the coal-gas mixtures show that they are much more transparent in the early stages of cooling and much less transparent after the temperature has fallen to below 1600° C. abs. than the hydrogen mixtures.

Table VIII.

Mean gas temperature ($^{\circ}$ C. abs.).	Intrinsic radiance from 59 cm. in vessel with black walls Intrinsic radiance from 30 cm. in vessel with black walls	
	25.4 per cent. hydrogen mixtures.	15 per cent. coal-gas mixtures.
2430	1.15	1.27
2400	1.15	1.25
2200	1.17	1.2
2000	1.17	1.14
1800	1.12	1.1
1600	1.1	1.08
1400	1.1	1.0 (nearly)
1200	1.1	1.0

* 'Phil. Trans.,' A, vol. 211, p. 397, Table XII.

Prof. Callendar experimenting with Méker burner flames has shown that the exponential law of absorption is closely obeyed in flame,* and following him I have shown that it is closely obeyed in exploded coal-gas mixtures contained in a closed vessel.† Assuming this law to hold for the hydrogen mixtures the coefficient of absorption has been calculated from intrinsic radiance measurements for 59 cm. and 30 cm. in the black vessel and tabulated in Table IX. The intrinsic radiance from an infinite thickness of the gaseous mixture (which in this case is the intrinsic radiance from a blackened cylindrical vessel of 30 cm. diameter and of very great length) has also been added. This has been calculated from the formula

$$R_{ix} = R_{i\infty} (1 - e^{-Kx})$$

where R_{ix} is the intrinsic radiance from x cm. of gas,‡

$R_{i\infty}$ is the intrinsic radiance from an infinite thickness and

K is the coefficient of absorption per cm.

Table IX.

Mean gas temperature (° C. abs.).	Intrinsic radiance in black vessel (cals. per sec.).			Coefficient of absorption, K .
	From 30 cm. (observed).	From 59 cm. (observed).	From infinite thickness (calculated).	
2440	6·9	7·95	8·1	0·062
2400	6·7	7·75	7·9	0·062
2200	5·8	6·2	6·4	0·06
2000	3·8	4·45	4·55	0·06
1800	2·6	2·9	2·95	0·72
1600	1·6	1·8	1·85	0·75

SUMMARY OF RESULTS.

The following are the main results obtained from these experiments:—

Part I.—When mixtures of hydrogen and air of various strengths at atmospheric density are exploded in the vessel when its walls are coated with a thin layer of dull black paint—

(i) the proportion of the heat of combustion lost by radiation during explosion and subsequent cooling decreases greatly with the mixture strength (see Table IV).

* ‘Third Report of British Association Committee on Gaseous Explosions,’ Appendix I.

† ‘Phil. Trans.,’ A, vol. 211, p. 401.

‡ As R_{ix} varies with the lateral dimensions as well as with the thickness, x , this formula only holds good for the gaseous mixture in a blackened cylindrical vessel of 30 cm. diameter and of varying length or thickness.

(ii) The total radiation emitted during explosion and subsequent cooling is a linear function of the maximum absolute temperature developed (see p. 187).

(iii) The proportion of the heat of combustion lost by radiation up to the moment of maximum temperature varied between 0.5 per cent. (for the strongest mixture experimented upon) and 1.4 per cent. (for the weakest mixture) (see Table V).

(iv) The maximum rate at which radiation is emitted occurs approximately at the point at which the temperature developed is a maximum (see p. 191).

(v) Weak mixtures radiate more powerfully in the initial stages of cooling than stronger mixtures when they have cooled to the same mean temperatures as the weaker mixtures have in this epoch (see fig. 5).

(vi) The rate of emission of radiation in the strongest mixture is approximately proportional to the fourth power of the absolute temperature of the gaseous mixture. This proportionality does not hold in the initial stages of cooling of the weak mixtures, but it holds satisfactorily in the later stages of cooling (see fig. 5).

(vii) The 2.8μ emission band of steam (hydrogen flame) ceases to be emitted in the hydrogen mixtures when the gas temperature has fallen to about 1000° C. abs. It would appear radiation of greater wave-length is emitted which contains appreciable energy at this temperature. At the highest temperatures in the 25.4 per cent. mixtures radiation of shorter wave-length than 2.8μ would appear to be emitted (see p. 192).

Part II.—The following results refer to experiments made in the vessel whose walls were silver-plated and therefore could be made either reflecting or absorbent as regards radiation—

(viii) The intrinsic radiance at any given temperature after explosion increases greatly as the reflecting power of the interior surface of the explosion vessel is increased; in other words, the intrinsic radiance at any given temperature increases with the size of the vessel (see p. 194).

(ix) The gaseous mixtures after explosion are very transparent throughout cooling to radiation of the same kind as they emit.

DISCUSSION OF RESULTS.

In discussing the results of the coal-gas and air experiments, it was pointed out that the energy in the vibratory degrees of freedom which gives rises to infra-red radiation appeared to be dependent upon density and volume as well as upon temperature.* The hydrogen experiments made in the reflecting vessel lend further support to the view that the vibratory energy is

* 'Phil. Trans.,' A, vol. 211, p. 410.

dependent upon volume as well as upon temperature. The effect of density in these mixtures was not investigated.

The experiments indicate that radiation phenomena in hydrogen mixtures are in general similar to those in coal-gas mixtures. In one or two respects, however, they show important differences, and these will here be briefly discussed.

As has been pointed out, the most noticeable difference lies in the fact that the rate of emission was not found to be a maximum during the explosion period, as was found to be the case in the coal-gas mixtures. That the rate of emission in the latter mixtures was greater during the explosion period (when the bulk of the chemical combination takes place) than at the moment of maximum temperature (when the bulk of chemical combination has been completed) was taken to support the theory that the energy of combination first passes (either wholly or in part) into the form of intramolecular energy, which is afterwards partitioned off in part into translational energy.* The hydrogen experiments do not appear to support this theory. A possible explanation is that combination between hydrogen and oxygen molecules is a simple transaction and may be completed within a time which might suitably be measured by molecular standards, whereas the combustion of hydrocarbon molecules may be a long-drawn-out process, which takes an appreciable time. In the light of this suggestion, it is clear that the volume of the hydrogen mixtures undergoing combination at any instant would be an infinitesimal fraction of the whole even during the period of greatest chemical activity, and consequently the influence of chemical activity on the radiation emitted (which comes from the whole mass of the gaseous mixture) would not be detected.

In another important respect do the hydrogen mixtures differ from the coal-gas mixtures. The proportion of the heat of combustion lost by radiation during explosion and subsequent cooling decreases with the mixture strength (and therefore with the maximum temperature developed) much more rapidly in the hydrogen mixtures than in the coal-gas mixtures. The explanation of this is pretty clear in the light of some experiments on the analysis of the radiation emitted in coal-gas and hydrogen mixtures.† The exploded weak hydrogen mixtures spend only a comparatively short period of their radiating history at temperatures at which they emit the $2.8\ \mu$ band (in which is concentrated the bulk of the radiation energy in these mixtures). The weak coal-gas mixtures, on the other hand, spend a considerable proportion of their

* 'Phil. Trans.,' A, vol. 211, p. 410.

† 'Phil. Mag.,' January, pp. 84-95 (1920).

history at radiating temperatures, both on account of their much slower cooling and also because they emit the strong $4.4\ \mu$ band of CO_2 , which continues to be emitted at temperatures at which the $2.8\ \mu$ band ceases to be emitted.

The experiments of Holborn and Henning on the specific heat of gases, although probably subject to a systematic error, as pointed out by Prof. Callendar,* show quite certainly that the rate of increase of the specific heat of steam increases very considerably with the temperature. Thus, over the temperature interval 100°C. – 600°C. it increases by about 4 per cent., while over the interval 600°C. – 1100°C. it increases by as much as 24 per cent. The quartz experiments would appear to throw some light on this. The emission spectrum of steam (hydrogen flame) consists essentially of a strong band at $2.8\ \mu$, and these experiments indicate that the energy in the vibratory degrees of freedom corresponding to radiation of this wave-length is not appreciable at temperatures below 700°C. (1000°C. abs.), but above this temperature these degrees begin to share to a rapidly increasing extent in the heat motion of the molecules.

The experiments described in this paper were all made in the Engineering Laboratory at Cambridge in the years previous to the war. The laboratory was then under the control of the late Prof. B. Hopkinson, and I desire to place on record my great indebtedness to him for the valuable advice and assistance he so readily gave me.

* Appendix to 'First Report of British Association Committee on Gaseous Explosions.'

The Aerodynamics of a Spinning Shell.

By R. H. FOWLER, E. G. GALLOP, C. N. H. LOCK, and H. W. RICHMOND, F.R.S.

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(Abstract.)

The paper to which this abstract is meant to serve as a non-technical introduction contains the results of work undertaken at the request of the Ordnance Committee and is published with their permission.

(1) *The Problems of Experimental External Ballistics.*—A spinning shell moving through the air is subjected in general to a complex reaction, which is determined primarily by its motion relative to the air. But a shell has an axis of symmetry, and when this axis of symmetry, its axis of rotation, and the direction of motion of its centre of gravity through the air all coincide the reaction naturally assumes its simplest form. When a shell is moving in such a manner it may be said to be moving "nose-on" through the air, and it is a matter of experience that, by giving a shell a suitable axial spin, it may be made to move practically nose-on through the air over very considerable distances. Under such conditions the symmetry clearly demands that the reaction of the air shall reduce to a single force, acting in the direction of motion reversed, which therefore merely tends to destroy the linear velocity of the shell, and a couple about the axis of symmetry, which tends to destroy the axial spin. The latter is comparatively unimportant, and it appears that, so long as the motion remains practically nose-on, the problem of determining the motion of the shell is reduced to one of particle dynamics, whose solution is now classical.

The object of all calculations of the motion of a shell is, of course, to determine, given the initial circumstances of projection, the position and velocity of the shell at any subsequent time. In order to complete this calculation in the simple case of nose-on motion we require a numerical knowledge of the one and only force component that matters—the drag, in aerodynamical terminology. This must be determined for a shell of the shape in use travelling nose-on at all velocities, through air in all conditions (all temperatures and densities). Once this determination has been made, the limited problem of nose-on motion may be regarded as completely solved.

Now we cannot calculate the drag *a priori*; its variation with velocity obeys no simple law, and can only be tabulated numerically by the analysis of observations, which can only be made of the initial motion of the shell over a fairly limited range. But by observation and analysis of initial

motions at various velocities we can determine the retardation, and so the drag, as a function of the velocity of the shell. We cannot control the air conditions and can at present only guess how they will affect the drag, but the guess is guided by the theory of dimensions and is probably fairly reliable. The required calculations of the motion can therefore be made.

The comparison of calculations and observations shows good agreement in range and height when the axial spin is suitable, and the total angle turned through by the tangent to the trajectory is less than (say) 50° . The calculated trajectory, however, is a curve lying in the vertical plane, containing the original direction of projection, while the observed positions of the shells do not lie in this plane, but appreciably to the right of it, when the axial spin is right-handed. This well-known departure from the original vertical plane is called *drift* and converts the trajectory into a twisted curve. It cannot be accounted for on the assumption of nose-on motion.

Particle dynamics thus fails to explain the drift, the phenomena of trajectories of large total curvature, and the behaviour of shells with unsuitable axial spin, with which is bound up the whole question of the stability of the nose-on motion and the angular oscillations of the axis, referred to later. In all such cases the assumption of nose-on motion breaks down and the directions of the axis and the motion of the centre of gravity of the shell no longer coincide. In such a case the angle between the two directions is called the *yaw*; the problem becomes one of rigid dynamics, and the general system of reactions on a yawed shell must be determined in order that it may be possible to submit to calculation the motion of the shell. The reaction on a yawed shell has never previously been studied experimentally, but a beginning has been made, with this object in view, in the experiments to be described in our paper, which are combined with a full theoretical discussion of the motion. We can, of course, as in the former case, only study experimentally the initial motion of the shell, but the information so obtained can be applied as before to the calculation of the whole trajectory.

(2) *Experiments on Yawed Shells.*—The experiments described deal with the flight of a 3-inch shell fired with velocities ranging from 900 f.s. to 2300 f.s. over a range of 600 feet from the muzzle of the gun. They are confined to the study of the angular oscillations of the axis of the shell relative to the direction of motion of the centre of gravity. It is shown that effects of gravity on the angular motion of the axis are negligible over this range, so that a shell with sufficient spin emerging from the muzzle of the gun with its axis at rest parallel to its direction of motion would retain such a position over the whole 600 feet. The possibility of these experiments therefore depends on the fact that the shell actually

receives a disturbance at the muzzle sufficient to give rise to angular oscillations of measurable amplitude.

The details of these oscillations are obtained by setting up a number of cardboard targets at right angles to the horizontal path of the shell, and measuring the shape of the resulting holes. If the axis of the shell is inclined to its direction of motion, the hole in the card will be elongated; the length of the longer axis of the hole determines the angle of yaw, δ , between the axis of the shell and its direction of motion; the orientation of the longer axis of the hole determines the azimuth ϕ of the plane containing the axis and direction of motion (the plane of yaw); these two co-ordinates determine the direction of the axis completely. It was found possible to make measurements of the direction of the axis with a probable error of about 0.2° . The instant of passing each card is also required, and this was obtained by determining the time interval between one or two pairs of chronograph screens, and interpolating by means of the standard air resistance tables for nose-on motion suitably modified. In this way the velocity of the shell at each point of the range was also obtained.

In analysing the results of the experiments, the equations of motion of a rigid body are applied to the spinning shell. The only forces acting are those impressed by the air (assuming that gravity may be neglected). So far as possible the equations of motion are solved with the various force components left as unknown functions. By comparing the solution with the observed motion of the shell, it is possible to deduce the magnitude of the various force components.

If a shell is moving at constant speed without angular velocity, the resultant force due to air resistance must by symmetry lie in the plane of yaw (fig. 1). It is convenient to resolve this into three components, as follows:—

Two force components through the centre of gravity—

- (i) The drag, R , in the direction of motion OP reversed;
- (ii) The cross-wind force, L , perpendicular to OP in the plane of yaw from P to A ;

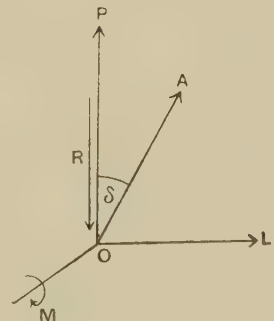


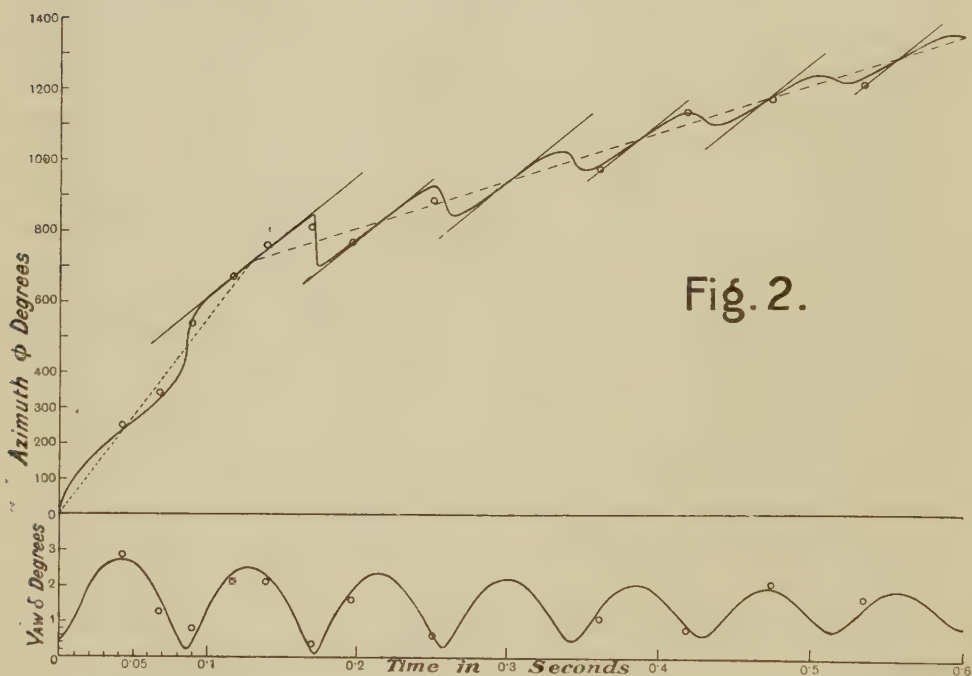
FIG. 1.

and the moment, M , of the resultant force about the centre of gravity tending to increase the yaw.

For an actual shell in flight the forces acting will be modified by the angular velocities. These modifications may be expected to be small.

The angular motion of the axis depends directly on the effect of the moment, M , and only indirectly on L and R through their effect in modifying the velocity and yaw on which M depends.

It is reasonable to assume, as a first approximation, that so far as M depends on the yaw, δ , it is proportional to $\sin \delta$ so long as δ is small. Writing $M = \mu \sin \delta$, we find that the periods of the angular oscillations of the shell depend only on μ and known data. For each round fired, the measured period of the oscillations determines a value of μ corresponding to the mean velocity of the shell down the range. The diminution of velocity over the range is too small to effect the value of μ appreciably, but by firing the shell at a number of different muzzle velocities the variation of μ with velocity is determined.



The determination of the moment, M , is the principal object of the experiments. It is determined as a function of v for two different types of shell over a range of velocities from 900 to 2300 f.s., and the results are supplemented by a determination in a wind channel which probably applies to velocities up to 700 f.s., and is consistent with the determination at other velocities. Rounds were fired from two guns with different riflings, the pitch being 1 turn in 30 diameters of the bore, and 1 in 40 respectively. The results from rounds with different spins were consistent and form a

valuable check on the accuracy of the method. The results comprise the only determination yet made of the moment of the fluid forces on a body moving at velocities at which the compressibility of the air produces marked effects.

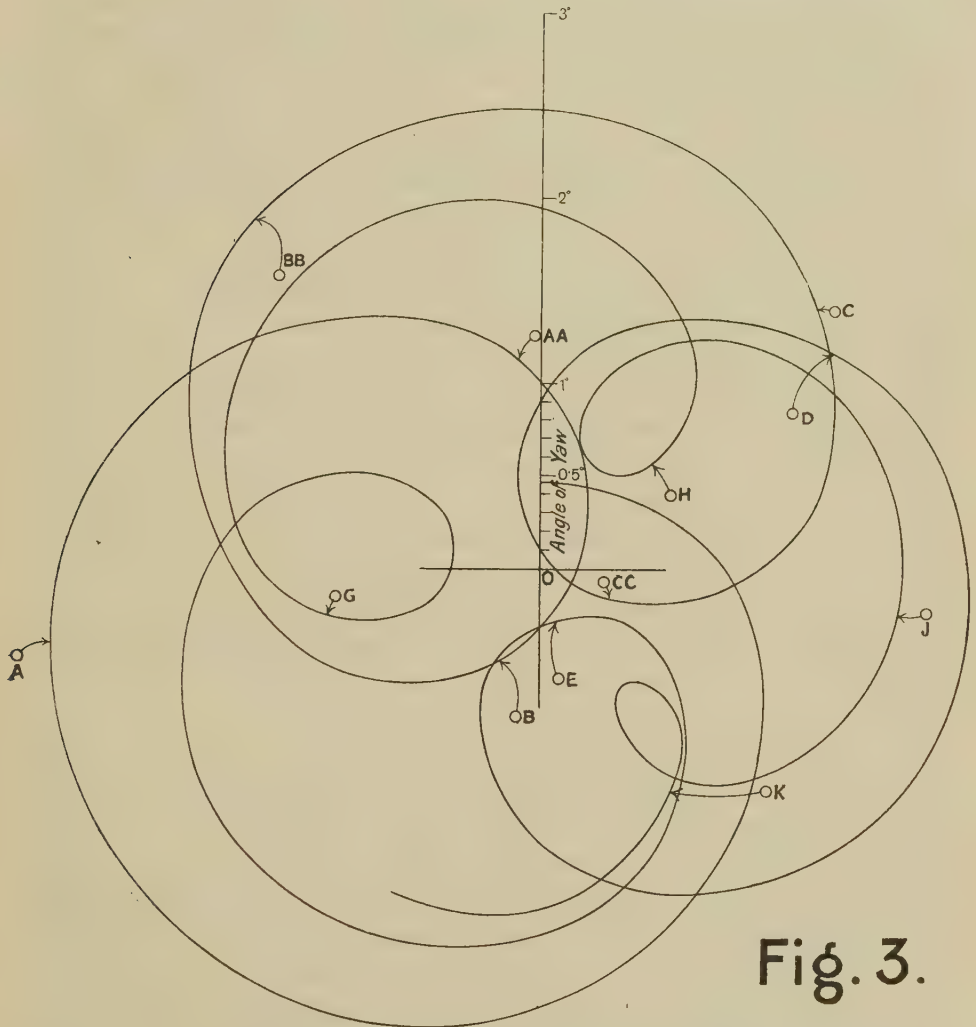


Fig. 3.

The curves show the *calculated* path of a point on the axis of the shell. The circles mark *observed* points on the path for Round I 24 of the full paper.

One of the two types of shell fired was loaded so as to give an extreme variation of the position of the centre of gravity of about 1 inch. From the resulting variation of the value of the moment, M , it was possible to reduce rough values for the cross-wind force, L , assuming that the drag

is known approximately. Details of the values of M and L obtained are given in the full paper.

It appears in the complete discussion that there is a close analogy between the motion of the spinning shell and that of a top under the action of gravity. The analogy is exact if μ is assumed constant and the direction of motion, OP , fixed. The angular velocities and moments of inertia of the shell about its centre of gravity correspond to those of a top about its point; the moment $\mu \sin \delta$ corresponds to the moment of gravity about the point of the top. In particular, the condition for the stability of small oscillations is the same for both. This result gives perhaps the most important practical application of the experiments, since a knowledge of μ makes it possible to determine the exact spin which must be given to a shell to make it stable.

In addition to the foregoing, some rough results were obtained as to the damping of the initial oscillations. These results are important, since a stable shell would be useless if the oscillations, which it inevitably possesses initially, were not rapidly damped out. The question is also of interest since the application of any sort of friction couple to a top, while tending to damp the oscillations of one period, always augments those of the other.* In the case of a shell, however, owing to the fact that the centre of gravity is not fixed, but can react to the forces generated by the axial oscillations, tracing out a spiral, this is not the case. Theory shows that a reasonable friction couple can be imagined to act, which, in combination with the spiral motion of the centre of gravity, will damp out the whole initial disturbance, in a manner agreeing, at least qualitatively, with the damping recorded in our experiments.

(3) *Comparison of Calculations and Observations.*—The result of a calculation, based on the theory we develop, is shown in fig. 2, where the angles δ and ϕ are plotted against the time, and in fig. 3, where the actual path of a point on the axis is shown with the angles δ and ϕ as polar co-ordinates. The values of the force components and the initial conditions were adjusted to fit the observations of each particular round, and the curves were then calculated from the theory. The observations of δ and ϕ are plotted for comparison. The average difference between the observed and calculated values of δ is in this case about 0.25° . Similar curves, drawn by eye to fit the observations in the process of analysing them, are given in the full paper. They are of exactly the same type as the calculated curve shown here.

In conclusion, we may repeat that, generally speaking, it is possible to calculate the exact motion of a shell over a complete trajectory with the help

* The small oscillations of a top near the vertical consist of a combination of terms of two distinct periods.

of the knowledge obtained from a full study of its initial motion. In particular, it can be shown that the curvature of the trajectory caused by gravity gives rise to a yaw of the axis of the shell to the right of the vertical plane containing the direction of projection (when the spin is right-handed), which increases along the trajectory. The cross-wind force caused by this yaw acts to the right and causes the drift mentioned above. Calculations of the drift based on the information obtained from these experiments have been made and found in fair agreement with the observed value.

The breakdown of the usual approximation of nose-on motion at the end of very long or sharply curved trajectories can also be studied by means of modified equations of motions suitable for the case in which the yaw and drift effects become large, provided the values of the corresponding force components have been obtained. This can be done by the analysis of initial motions in which the shells are almost or quite unstable, and large values of the yaw are developed in consequence. Such observations have been made, but their analysis has not yet been carried out. In practice, however, large values of the yaw do not in general occur until the velocity of the shell has fallen to a low value, so that this case is largely covered by wind-channel experiments.

On the Vibrations of an Elastic Plate in Contact with Water.

By HORACE LAMB, F.R.S.

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In connection with the problem of submarine signalling the question arose as to the pitch of the fundamental note of a thin circular plate or diaphragm of given material and dimensions, filling an aperture in a plane wall which is in contact on one side with an otherwise unlimited mass of water. The following investigation, which includes some extensions, is now published by permission.

To simplify the theoretical treatment, the wall is supposed to be rigid, and the plate to be firmly clamped to it along the circumference, although these conditions are only imperfectly fulfilled in practice. Even with these limitations an exact solution is out of the question, but a sufficient approximation can be obtained by Rayleigh's method of an assumed type,* which gives good results if the type be suitably chosen. It is known that the frequency estimated in this way will be somewhat too high.

* 'Theory of Sound,' § 90.

1. If h be the thickness of the plate, E the value of Young's modulus for the material, and μ Poisson's ratio, the potential energy is*

$$V = \frac{Eh^3}{24(1-\mu^2)} \iint \left(\frac{1}{R_1^2} + \frac{2\mu}{R_1 R_2} + \frac{1}{R_2^2} \right) dS, \quad (1)$$

where dS is an element of area, and R_1^{-1} , R_2^{-1} are the principal curvatures of this element. For a plate clamped at the edge the integral curvature

$$\iint \frac{dS}{R_1 R_2}$$

obviously vanishes, and the integrand in (1) may therefore be replaced by

$$\left(\frac{1}{R_1} + \frac{1}{R_2} \right)^2. \quad (2)$$

If w be the normal displacement at a distance r from the centre, the boundary conditions are $w = 0$, $\partial w / \partial r = 0$ for $r = a$, the radius of the aperture. The simplest assumption consistent with these conditions, and with the obvious requirement that $\partial w / \partial r = 0$ for $r = 0$, is

$$w = C \left(1 - \frac{r^2}{a^2} \right)^2, \quad (3)$$

where C is a function of t only. This makes

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{\partial^2 w}{\partial r^2} + \frac{1}{r} \frac{\partial w}{\partial r} = \frac{8C}{a^2} \left(1 - 2 \frac{r^2}{a^2} \right),$$

and thence

$$V = \frac{8\pi E h^3}{9(1-\mu^2)a^2} C^2. \quad (4)$$

The kinetic energy of the plate is

$$T_1 = \pi \rho_1 h \int_0^a \left(\frac{\partial w}{\partial t} \right)^2 r dr = \frac{\pi \rho_1 h a^3}{10} \left(\frac{dC}{dt} \right)^2, \quad (5)$$

where ρ_1 is the density.

Hence if the water were absent, and the plate were constrained to vibrate in the form (3), the frequency ($p/2\pi$) would be given by

$$p^2 = \frac{80}{9} \frac{h^2 c_1^2}{a^4}, \quad (6)$$

where

$$c_1^2 = \frac{E}{(1-\mu^2)\rho_1}, \quad (7)$$

i.e., c_1 is the velocity of propagation of extensional waves in an infinite thin plate of the same material and thickness. Hence

$$\frac{p}{2\pi} = 0.4745 \frac{h c_1}{a^2}. \quad (8)$$

* Rayleigh, § 214.

The vibrations of a clamped circular plate *in vacuo* have been discussed by F. Meyer zur Capellen,* whose numerical results give, for the gravest symmetrical mode,

$$\frac{p}{2\pi} = 0.4693 \frac{hc_1}{a^2}. \quad (9)$$

Our approximation, therefore, gives a frequency which is too high by about 1 per cent. An improved approximation, given below in §7, agrees almost exactly with the true value.

For an iron plate, assuming

$$E = 2 \times 10^{12}, \quad \rho_1 = 7.8, \quad \mu = \frac{1}{4} \quad (\text{C.G.S.}),$$

we have

$$c_1 = 5.230 \times 10^5 \text{ cm./sec.},$$

and thence from (8)

$$\frac{p}{2\pi} = 2.481 \frac{h}{a^2} \times 10^5. \quad (10)$$

To take a practical example, for a plate 7 inches (= 17.5 cm.) in diameter and $\frac{1}{8}$ -inch thick, the formula (8) makes

$$p/2\pi = 1013. \quad (11)$$

2. The presence of the water, in our problem, has the effect, first of lowering the frequency on account of the increased inertia, and secondly of damping the vibrations owing to the energy carried off in the form of sound-waves.

If (as we assume) the wave-length is considerable as compared with the diameter of the plate the former effect is practically the same as if the water were incompressible. On this supposition the velocity-potential at any point of the water is

$$\phi = -\frac{1}{2\pi} \iint \frac{\partial \phi}{\partial n} \frac{dS}{r'} = \frac{1}{2\pi} \iint \frac{\partial w}{\partial t} \frac{dS}{r'}, \quad (12)$$

where r' is the distance of the point in question from the element dS of the plate. This is identical with the electric-potential of a plate of surface-density $\dot{w}/2\pi$. Now by a known formula† the potential of a disk of surface-density

$$\left(1 - \frac{r^2}{a^2}\right)^n$$

at points of the disk itself is

$$\frac{\pi^{\frac{1}{2}} \Pi(n)}{\Pi(n + \frac{1}{2})} F\left(-n - \frac{1}{2}, \frac{1}{2}, 1, \frac{r^2}{a^2}\right) a$$

in Gauss' hypergeometric notation.

* 'Ann. d. Physik,' vol. 33 (1888). See also Rayleigh, § 221a.

† 'Roy. Soc. Proc.,' vol. 42, pp. 290, 291, where reference is made to Ferrers, 'Quart. Journ. Math.,' vol. 14.

Hence if for greater generality we write for a moment

$$w = C \left(1 - \frac{r^2}{a^2}\right)^n, \quad (13)$$

the velocity-potential at the surface of the disk is*

$$\phi = \frac{\pi^{\frac{1}{2}} \Pi(n)}{2 \Pi(n + \frac{1}{2})} F\left(-n - \frac{1}{2}, \frac{1}{2}, 1, \frac{r^2}{a^2}\right) a \frac{dC}{dt}. \quad (14)$$

The kinetic energy of the water is therefore

$$\begin{aligned} T_2 &= -\frac{1}{2} \rho \iint \phi \frac{\partial \phi}{\partial n} dS = \frac{1}{2} \rho \iint \phi \frac{\partial w}{\partial t} dS \\ &= \frac{\pi^{\frac{1}{2}} \Pi(n)}{2 \Pi(n + \frac{1}{2})} \rho a \left(\frac{dC}{dt}\right)^2 \int_0^a F\left(-n - \frac{1}{2}, \frac{1}{2}, 1, \frac{r^2}{a^2}\right) \left(1 - \frac{r^2}{a^2}\right)^n r dr. \end{aligned} \quad (15)$$

It is easily proved that

$$\int_0^1 F(\alpha, \beta, 1, z) (1-z)^n dz = \frac{F_1(\alpha, \beta, n+2)}{n+1} = \frac{\Pi(n) \Pi(n+1-\alpha-\beta)}{\Pi(n+1-\alpha) \Pi(n+1-\beta)}. \quad (16)$$

Hence, putting $\alpha = -n - \frac{1}{2}$, $\beta = \frac{1}{2}$, the formula (15) becomes

$$T_2 = \frac{1}{4} \left\{ \frac{\Pi(n)}{\Pi(n + \frac{1}{2})} \right\}^2 \frac{\Pi(2n+1)}{\Pi(2n + \frac{3}{2})} \pi^{\frac{1}{2}} \rho a^3 \left(\frac{dC}{dt}\right)^2. \quad (17)$$

By way of verification we may put $n = 0$, which makes

$$T_2 = \frac{4}{3} \rho a^3 \left(\frac{dC}{dt}\right)^2. \quad (18)$$

This is the case of a *rigid* disk oscillating in a circular aperture.† Again, if $n = -\frac{1}{2}$ we have

$$T_2 = \frac{1}{2} \pi^2 \rho a^3 \left(\frac{dC}{dt}\right)^2, \quad (19)$$

which may also be verified by comparison with a known electrical result.

For the present purpose we put $n = 2$, which makes

$$T_2 = 0.4203 \times \frac{1}{2} \rho a^3 \left(\frac{dC}{dt}\right)^2. \quad (21)$$

The effect of the water is virtually to increase the inertia in the ratio $(T_1 + T_2)/T_1$, or $1 + \beta$, say, where

$$\beta = 0.6689 \frac{\rho}{\rho_1} \frac{a}{h}. \quad (22)$$

The frequency is lowered in the ratio $(1 + \beta)^{-\frac{1}{2}}$, and is therefore, by (8),

$$\frac{\rho}{2\pi} = \frac{0.4745}{\sqrt{(1 + \beta)}} \frac{h c_1}{a^2}. \quad (23)$$

* Another derivation of this formula is given at the end of the paper.

† Rayleigh, § 302.

For an iron plate of the dimensions chosen in §1 we have $\beta = 2.401$. The frequency is lowered in the ratio 0.542, and is accordingly now about 550.

The preceding calculation relates only to the gravest mode of vibration, where the whole surface of the plate is at any instant in the same phase. In the case of a bell, or of a plate vibrating in segments separated by nodal lines, the effect of the inertia of the water will be less, owing to the freedom of lateral motion near the surface, between adjacent segments in opposite phases.

3. To estimate the rate of damping we must calculate the emission of energy in the form of sound-waves. If we put

$$\frac{dC}{dt} = A \cos pt, \quad (24)$$

the integral of the normal velocity over the surface of the plate is

$$\int_0^a \frac{\partial w}{\partial t} 2\pi r dr = 2\pi \frac{dC}{dt} \int_0^a \left(1 - \frac{r^2}{a^2}\right)^2 r dr = \frac{1}{3} \pi a^2 A \cos pt. \quad (25)$$

The effect at a distance is, therefore, that of a simple source, of strength $\frac{2}{3} \pi a^2 A$. The mean rate at which energy is carried outwards by the hemispherical waves is therefore*

$$\frac{p^2 \rho}{16 \pi c} \left(\frac{2}{3} \pi a^2 A\right)^2 = \frac{\pi p^2 \rho a^4}{36 c} A^2, \quad (26)$$

where c is the velocity of sound in the water.

The mean energy of the plate and adjacent water, being twice the mean kinetic energy, is

$$\frac{1}{10} \pi \rho_1 h a^2 (1 + \beta) A^2. \quad (27)$$

Equating the rate of decay of the energy to the emission we find

$$\frac{dA}{dt} = -\alpha A, \quad (28)$$

where

$$\alpha = \frac{5}{36} \frac{\rho}{\rho_1} \frac{p^2 a^2}{(1 + \beta) h c}. \quad (29)$$

The amplitude diminishes according to the law $e^{-\alpha t}$.

The importance of the damping is best estimated in relation to the frequency. The degree of persistence of the vibrations is indicated by the number of vibrations which elapse while the amplitude diminishes in the ratio $1/e$, viz., $p/2\pi\alpha$. Referring to (23) we find

$$\frac{p}{2\pi\alpha} = 0.385 (1 + \beta)^{\frac{1}{2}} \frac{\rho_1 c}{\rho c_1}. \quad (30)$$

The dimensions of the plate only occur here through the value of β .

* Rayleigh, § 280.

Putting $c = 1.435 \times 10^5$, $\rho_1/\rho = 7.8$,

we find for an iron plate

$$p/2\pi\alpha = 0.823(1 + \beta)^{\frac{1}{2}}, \quad (31)$$

and thence for the particular plate described in § 1

$$p/2\pi\alpha = 5.16. \quad (32)$$

In spite of the small persistence thus indicated, the vibrations are far from being "dead beat." The damping, though considerable, is not sufficient to affect the frequency appreciably, this influence being always of the order α^2/p^2 , which is less than $1/1000$ in the present case. There is also a considerable degree of selective resonance to external sources of sound. The general rule is that the energy of resonance falls to one-half the maximum when the frequency of the source differs from the natural frequency of the resonator by the fraction α/p , approximately. Thus in the above example, where the frequency (as modified by the water) is about 550, the range over which the energy will exceed half the maximum is confined between the limits 530 and 570, approximately.

In all cases the persistence of the vibrations (as measured in periods) will be greater, and the resonance will attain a greater maximum, and at the same time be more concentrated, the thinner the plate.

The preceding calculation assumes, of course, that the loss of energy is wholly due to the sound-waves generated in the water. The effect of viscosity is unimportant, but in practice some energy will be lost by vibrations communicated to the wall in which the plate is fixed.

4. The gravest mode of vibration with a *nodal diameter* admits of a similar approximation, and the comparison has points of interest. Taking polar co-ordinates in the plane of the diaphragm we have

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{\partial^2 w}{\partial r^2} + \frac{1}{r} \frac{\partial w}{\partial r} + \frac{1}{r^2} \frac{\partial^2 w}{\partial \theta^2}. \quad (33)$$

Assuming

$$w = C \left(1 - \frac{r^2}{a^2}\right)^2 r \cos \theta, \quad (34)$$

we find

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{C}{a^2} \left(-16 + 24 \frac{r^2}{a^2}\right) r \cos \theta, \quad (35)$$

and thence

$$V = \frac{\pi E h^3}{3(1 - \mu^2)} C^2. \quad (36)$$

The kinetic energy of the plate is

$$T_1 = \frac{1}{2} \rho_1 h \iint \left(\frac{\partial w}{\partial t}\right)^2 r d\theta dr = \frac{\pi \rho_1 h a^4}{120} \left(\frac{dC}{dt}\right)^2. \quad (37)$$

Hence if the water be absent the frequency corresponding to our assumed type is determined by

$$p^2 = 40 \frac{h^2 c_1^2}{a^4}, \quad (38)$$

or
$$\frac{p}{2\pi} = 1.0066 \frac{hc_1}{a^2}. \quad (39)$$

A closer approximation, given in § 9 below, shows that this result is about 3 per cent. too high. For an iron plate (39) makes

$$p/2\pi = 5.26 \times 10^5 \times \frac{h}{a^2}, \quad (40)$$

which may be compared with (10).

5. To allow for the inertia of the water we proceed as in § 2.

The potential of a disk of density

$$\left(1 - \frac{r^2}{a^2}\right)^n x$$

at points of the disk itself is

$$\frac{\pi^2 a \Pi(n)}{2 \Pi(n + \frac{1}{2})} F\left(-n - \frac{1}{2}, \frac{3}{2}, 2, \frac{r^2}{a^2}\right) x. \quad (41)^*$$

Hence, putting $x = r \cos \theta$ and referring to (12), the velocity-potential at the surface of the disk, in our problem, is

$$\phi = \frac{4a}{15} \frac{dC}{dt} F\left(-\frac{5}{2}, \frac{3}{2}, 2, \frac{r^2}{a^2}\right) r \cos \theta. \quad (42)$$

The kinetic energy of the adjacent water is therefore

$$T_2 = \frac{2\pi\rho a}{15} \left(\frac{dC}{dt}\right)^2 \int_0^a F\left(-\frac{5}{2}, \frac{3}{2}, 2, \frac{r^2}{a^2}\right) \left(1 - \frac{r^2}{a^2}\right)^2 r^3 dr. \quad (43)$$

It may be shown without difficulty that

$$\int_0^1 F(\alpha, \beta, 2, z) (1-z)^n z dz = \frac{F_1(\alpha, \beta, n+3)}{(n+1)(n+2)} = \frac{\Pi(n) \Pi(n+2-\alpha-\beta)}{\Pi(n+2-\alpha) \Pi(n+2-\beta)}. \quad (44)$$

Hence, putting $n = 2$, $\alpha = -\frac{5}{2}$, $\beta = \frac{3}{2}$, we find after a little arithmetic

$$T_2 = 0.008083 \rho a^5 \left(\frac{dC}{dt}\right)^2. \quad (45)$$

The frequency is therefore reduced by the inertia of the water in the ratio $(1+\beta)^{-\frac{1}{2}}$, where

$$\beta = T_2/T_1 = 0.3087 \frac{\rho a}{\rho_1 h}. \quad (46)$$

* This is obtained by differentiation of (13) and (14) with respect to x . A correction on account of the boundary vanishes in the present case. Cf. Ferrers, *loc. cit.*

For the particular disk above specified, the ratio is 0.688, as against 0.542 for the gravest symmetrical mode.

6. To calculate the emission of energy, we require the value of the velocity-potential at a great distance R from the centre of the diaphragm. This is given by the integral

$$\phi = \frac{1}{2\pi} \iint \frac{e^{-ikr'}}{r'} \frac{\partial w}{\partial t} dS, \quad (47)$$

where $k = p/c$, taken over the area of the plate.* Here r' denotes the distance of the point considered, whose spherical polar co-ordinates are (say) R, χ, ψ , from the element dS whose polar co-ordinates *in plano* are r, θ . Hence

$$\begin{aligned} r' &= \{R^2 - 2Rr \sin \chi \cos(\psi - \theta) + r^2\}^{\frac{1}{2}}, \\ &= R - r \sin \chi \cos(\psi - \theta), \end{aligned} \quad (48)$$

approximately, and therefore

$$e^{-ikr'} = e^{-ikR} \{1 + ikr \sin \chi \cos(\psi - \theta)\}. \quad (49)$$

Hence if

$$\frac{\partial w}{\partial t} = \left(1 - \frac{r^2}{a^2}\right)^2 r \cos \theta A e^{ikct}, \quad (50)$$

the value of ϕ at a great distance R is

$$\begin{aligned} \phi &= \frac{A e^{ik(ct-R)}}{2\pi R} \int_0^{2\pi} \int_0^a \{1 + ikr \sin \chi \cos(\psi - \theta)\} \left(1 - \frac{r^2}{a^2}\right)^2 r^2 \cos \theta d\theta dr \\ &= \frac{ika^4}{48R} A e^{ik(ct-R)} \sin \chi \cos \psi. \end{aligned} \quad (51)$$

Taking the real part, we have

$$\phi = -\frac{ka^4}{48R} A \sin k(ct-R) \sin \chi \cos \psi \quad (52)$$

corresponding to the normal velocity

$$\frac{\partial w}{\partial t} = \left(1 - \frac{r^2}{a^2}\right)^2 r \cos \theta \cdot A \cos kct. \quad (53)$$

The flux of energy across a hemispherical surface of radius R is

$$-\int_0^{2\pi} \int_0^{\frac{1}{2}\pi} \rho \frac{\partial \phi}{\partial t} \frac{\partial \phi}{\partial R} R^2 \sin \chi d\chi d\psi. \quad (54)$$

Substituting from (52), and taking the mean value with respect to the time, we obtain

$$\frac{\pi k^4 a^8 \rho c}{6912} A^2. \quad (55)$$

* Rayleigh, § 278.

The mean energy is

$$\frac{\pi \rho_1 h a^4}{120} (1 + \beta) A^2, \quad (56)$$

where β is given by (46). The argument of § 3 then shows that the amplitude diminishes according to the law $e^{-\alpha t}$, where

$$\alpha = \frac{5}{576} (1 + \beta)^{-1} k^4 a^4 \frac{\rho c}{\rho_1 h}. \quad (57)$$

Since $k = p/c$, and

$$p^2 = \frac{40}{1 + \beta} \frac{h^2 c_1^2}{a^4}, \quad (58)$$

we find

$$\frac{p}{2\pi\alpha} = 0.0725 (1 + \beta)^{\frac{1}{2}} \frac{\rho_1 c^3 a^2}{\rho c_1^3 h^2}. \quad (59)$$

For an iron plate of the special dimensions above given, this makes

$$p/2\pi\alpha = 59.4, \quad (60)$$

which may be contrasted with (32).

7. The approximations of §§ 1-3 are probably near enough for any practical purpose, regard being had to the variations in the values of E and ρ_1 for the same material, and the difficulty in securing the ideal condition of clamping. It may be of some interest, however, to show how the approximations may be improved.

Considering, first, the symmetrical vibrations, we assume, in place of (3),

$$w = C \left\{ \left(1 - \frac{r^2}{a^2} \right)^2 + \lambda \left(1 - \frac{r^2}{a^2} \right)^3 \right\}, \quad (61)$$

where λ is as yet undetermined. The consequent value of the potential energy of the plate is

$$V = \frac{8\pi E h^3}{9(1 - \mu^2)a^2} \left(1 + \frac{3}{2}\lambda + \frac{9}{10}\lambda^2 \right) C^2. \quad (62)$$

The kinetic energy of the plate alone is

$$T_1 = \frac{\pi \rho_1 h a^2}{10} \left(1 + \frac{5}{3}\lambda + \frac{5}{7}\lambda^2 \right) \left(\frac{dC}{dt} \right)^2. \quad (63)$$

Hence, for the plate when vibrating *in vacuo* according to the constrained type (61)

$$p^2 = \frac{56}{3} \cdot \frac{10 + 15\lambda + 9\lambda^2}{21 + 35\lambda + 15\lambda^2} \cdot \frac{h^2 c_1^2}{a^4}. \quad (64)$$

Since this is, in any case, an over-estimate for the gravest mode, we choose λ so as to make the second fraction a minimum. Now the stationary values of the function

$$u = \frac{a + 2h\lambda + b\lambda^2}{A + 2H\lambda + B\lambda^2} \quad (65)$$

are given by the quadratic

$$(AB - H^2)u^2 - (aB + bA - 2Hh)u + ab - h^2 = 0, \quad (66)$$

which in our case reduces to

$$35u^2 - 306u + 135 = 0. \quad (67)$$

The roots of this are

$$u = 0.46602, \quad 8.2768. \quad (68)$$

The former of these makes

$$\frac{p}{2\pi} = 0.4694 \frac{hc_1}{a^2} \quad (69)$$

which is practically the correct value.

The second of the roots (68) gives a rough approximation for that mode of symmetrical vibration in which there is a nodal circle. It makes

$$\frac{p}{2\pi} = 1.978 \frac{hc_1}{a^2}, \quad (70)$$

the correct numerical factor being about 1.827.

8. When allowance is to be made for the inertia of the water, the improved calculation becomes rather intricate. The leading steps only are given in what follows.

The velocity-potential at the disk is

$$\phi = \frac{\pi^{\frac{1}{2}}}{2} \left\{ \frac{\Pi(2)}{\Pi(\frac{5}{2})} F\left(-\frac{5}{2}, \frac{1}{2}, 1, \frac{r^2}{a^2}\right) + \lambda \frac{\Pi(3)}{\Pi(\frac{7}{2})} F\left(-\frac{7}{2}, \frac{1}{2}, 1, \frac{r^2}{a^2}\right) \right\} a \frac{dC}{dt}, \quad (71)$$

by (14). To find the kinetic energy of the water we must multiply this expression by

$$\pi\rho \left\{ \left(1 - \frac{r^2}{a^2}\right)^2 + \lambda \left(1 - \frac{r^2}{a^2}\right)^3 \right\} \frac{dC}{dt} r dr,$$

and integrate from $r = 0$ to $r = a$. The result, obtained with the help of (16), is

$$\begin{aligned} T_2 = \frac{\pi^{\frac{1}{2}}\rho a^3 \left(\frac{dC}{dt}\right)^2}{4} & \left\{ \frac{\Pi(2)}{\Pi(\frac{5}{2})} \cdot \frac{\Pi(2)\Pi(5)}{\Pi(\frac{5}{2})\Pi(\frac{1}{2})} + \lambda \frac{\Pi(3)}{\Pi(\frac{7}{2})} \cdot \frac{\Pi(2)\Pi(6)}{\Pi(\frac{5}{2})\Pi(\frac{1}{2})} \right. \\ & \left. + \lambda \frac{\Pi(2)}{\Pi(\frac{5}{2})} \cdot \frac{\Pi(3)\Pi(6)}{\Pi(\frac{7}{2})\Pi(\frac{1}{2})} + \lambda^2 \frac{\Pi(3)}{\Pi(\frac{7}{2})} \cdot \frac{\Pi(3)\Pi(7)}{\Pi(\frac{7}{2})\Pi(\frac{1}{2})} \right\}, \quad (72) \end{aligned}$$

or
$$T_2 = 0.21015 \left(1 + \frac{1.44}{91}\lambda + \frac{2.88}{455}\lambda^2\right) \rho a^3 \left(\frac{dC}{dt}\right)^2. \quad (73)$$

Hence, referring to (62) and (63)

$$p^2 = \frac{3.0}{9} \cdot \frac{1 + \frac{3}{2}\lambda + \frac{9}{10}\lambda^2}{1 + \frac{5}{3}\lambda + \frac{5}{7}\lambda^2 + 0.66894 \frac{\rho a}{\rho_1 h} \left(1 + \frac{1.44}{91}\lambda + \frac{2.88}{455}\lambda^2\right)} \frac{h^2 c_1^2}{a^4}. \quad (74)$$

The minimum value of the second fraction has to be determined for each case separately. In the example already used for illustration we have $\rho_1/\rho = 7.8$, $a/h = 28$, and therefore $0.6689\rho a/\rho_1 h = 2.401$. The fraction in question has then the form (65) with

$$\begin{aligned} a &= 1, & h &= 0.75, & b &= 0.9, \\ A &= 3.4013, & H &= 2.7333, & B &= 2.2342. \end{aligned}$$

The equation to find the stationary values of u is

$$0.1250u^2 - 1.195u + 0.3375 = 0, \quad (75)$$

$$\text{whence} \quad u = 0.2914, \quad 9.03. \quad (76)$$

The lower root makes

$$\frac{p}{2\pi} = 0.2562 \frac{hc_1}{a^2}. \quad (77)$$

The frequency is therefore reduced by the inertia of the water in the ratio 0.546, which differs only slightly from the result found by the simpler method.

9. For the gravest mode with a nodal diameter we may assume

$$w = C \left\{ \left(1 - \frac{r^2}{a^2} \right)^2 + \lambda \left(1 - \frac{r^2}{a^2} \right)^3 \right\} x. \quad (78)$$

This makes

$$V = \frac{\pi E h^3}{3(1-\mu^2)} \left(1 + \frac{6}{5}\lambda + \frac{3}{5}\lambda^2 \right) C^2, \quad (79)$$

$$T_1 = \frac{\pi \rho_1 h a^4}{120} \left(1 + \frac{10}{7}\lambda + \frac{15}{8}\lambda^2 \right) \left(\frac{dC}{dt} \right)^2. \quad (80)$$

Hence, for the plate vibrating *in vacuo*,

$$p^2 = 40 \frac{1 + \frac{6}{5}\lambda + \frac{3}{5}\lambda^2}{1 + \frac{10}{7}\lambda + \frac{15}{8}\lambda^2} \frac{h^2 c_1^2}{a^4} = 224 \cdot \frac{5 + 6\lambda + 3\lambda^2}{28 + 40\lambda + 15\lambda^2} \cdot \frac{h^2 c_1^2}{a^4}. \quad (81)$$

The minimum value of the fraction is 0.1684, whence

$$\frac{p}{2\pi} = 0.978 \frac{hc_1}{a^2}. \quad (82)$$

The effect of the inertia of the water may be worked out as in §8, but it is hardly worth while to reproduce the details. I find that the frequency is reduced in the ratio 0.694, which differs little from the value previously found.

Note.—The result quoted immediately after equation (12) was deduced from Ferrers' work on the potentials of heterogeneous ellipsoids. An independent proof of the formula (14) to which it leads may be given in terms of Bessel's functions.

If the distribution of normal velocity over the disk be

$$\frac{\partial w}{\partial t} = \left(1 - \frac{r^2}{a^2}\right)^n \frac{dC}{dt}, \quad (83)$$

the velocity-potential on the positive side is*

$$\phi = \int_0^\infty e^{-kz} J_0(kr) dk \int_0^a J_0(kr') \left(1 - \frac{r'^2}{a^2}\right)^n r' dr' \cdot \frac{dC}{dt}, \quad (84)$$

where z denotes distance from the plane of the disk.

Expanding $J_0(kr')$, and writing $r' = a \sin \phi$, we find

$$\int_0^a J_0(kr') \left(1 - \frac{r'^2}{a^2}\right)^n r' dr' = \frac{2^n \Pi(n) a^2}{(ka)^{n+1}} J_{n+1}(ka) \quad (85)$$

Again we have†

$$\int_0^\infty J_0(kr) J_{n+1}(ka) \frac{d(ka)}{(ka)^{n+1}} = \frac{\sqrt{\pi} \Pi(n)}{2 \Pi(n + \frac{1}{2})} F\left(-n - \frac{1}{2}, \frac{1}{2}, 1, \frac{r^2}{a^2}\right). \quad (86)$$

Hence, putting $z = 0$ in (84) we have the formula (14).

The Transmission of Electric Waves around the Earth's Surface.

By H. M. MACDONALD, F.R.S.

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In a previous communication‡ the law of decrease of the amplitude of the magnetic force of a train of electric waves emitted from a simple oscillator at the surface of a perfectly conducting sphere as the distance of the receiver (also on the surface) from the oscillator increases was investigated, and in a later communication§ the effect of imperfect conduction was discussed. The method adopted consisted (1) in showing that the terms of the series for ψ where

$$\psi = \kappa z_1^{-2} \sum_1^\infty (2n+1) z_1^{1/2} K_{n+1/2}(\iota z_1) (1 - \mu^2) \frac{dP_n}{d\mu} \bigg| \frac{\partial}{\partial z_0} \{z_0 K_{n+1/2}(\iota z_0)\},$$

which contributed the principal part of ψ were those for which $|n + \frac{1}{2} - z_0|$

* 'Hydrodynamics,' 1916, p. 130.

† See Nielsen, 'Theorie der Cylinderfunktionen,' p. 193, or Schafheitlein, 'Theorie der Bessel'schen Funktionen,' p. 76.

‡ 'Roy. Soc. Proc.,' A, vol. 90, p. 50 (1914).

§ 'Roy. Soc. Proc.,' A, vol. 92, p. 493 (1916).

is of the same or lower order than $z_0^{1/3}$,* (2) in showing that the corresponding part of the series for ψ can be replaced by the series

$$-\kappa z_0^{-2} \sum 3^{-1/3} z_0^{1/3} (2n+1) \xi^{1/3} K_{1/3}(\xi e^{-\pi i}) (1-\mu^2) \frac{dP_n}{d\mu} / \xi^{2/3} K_{2/3}(\xi e^{-\pi i}),$$

where $\xi = 2\zeta^{3/2}$, $3\zeta = 6^{1/3} z_0^{-1/3} (n + \frac{1}{2} - z_0)$,

and the summation extends from some value of n for which $z_0 - (n + \frac{1}{2})$ is of the same order as $z_0^{1/3}$ to some value of n for which $n + \frac{1}{2} - z_0$ is of the same order as $z_0^{1/3}$; (3) in expressing $\xi^{1/3} K_{1/3}(\xi e^{-\pi i}) / \xi^{2/3} K_{2/3}(\xi e^{-\pi i})$ as a sum of partial fractions of the form $A_k / (\xi^{2/3} - \xi_k^{2/3})$, which is possible since $\xi^{1/3} K_{1/3}(\xi e^{-\pi i})$ and $\xi^{2/3} K_{2/3}(\xi e^{-\pi i})$ are both integral functions of $\xi^{2/3}$ and, as is shown, the zeros of $\xi^{2/3} K_{2/3}(\xi e^{-\pi i})$ are simple zeros; (4) in obtaining the principal part of the sum of the series by replacing the sum with regard to n by an integral, as this gives the sum of the parts of the terms which are oscillating most slowly; (5) in showing that the effect of the terms in the original series for ψ for which $|n + \frac{1}{2} - z_0|$ is of higher order than $z_0^{1/3}$ is negligible in comparison with the principal part thus obtained.

The result showed that the decrease of amplitude with increase of distance from the oscillator was of a magnitude which made the amplitude practically insensible for the wave-lengths in use in wireless telegraphy at distances on the earth's surface from the oscillator greater than those for which the approximation used in the analysis for Legendre's function $P_n(\mu)$, viz., $J_0\{(2n+1)\sin\frac{1}{2}\theta\}$ is a sufficient approximation. As will appear later the appropriate expressions for the magnetic and electric forces at any point on the surface can be obtained by the same methods as in the previous investigations, but it may be observed that the expressions at a great distance from the oscillator are not of practical interest.

The problem of the transmission of electric waves on the earth's surface has been discussed by Prof. G. N. Watson,† the method adopted by him being to replace the series by a sum of residues by means of a contour integral.‡ The discussion of this sum of residues proceeds on the assumption that it can be arranged as a simple converging series, but the treatment would appear to be inadequate. It may be pointed out that the existence of zeros of a function cannot be demonstrated by the use of an asymptotic expression, as all that could be proved in this way is that the value of the modulus of the function decreases to a value less than some given value, not that it actually vanishes.

* This also follows from a previous investigation, 'Roy. Soc. Proc.,' vol. 72, p. 59 (1904).

† 'Roy. Soc. Proc.,' A, vol. 95, p. 83 (1918).

‡ The replacement of a series in this manner appears to be originally due to Cauchy, and has been used by other writers, but it may be observed that the sum which replaces the series is in general less amenable to treatment than the original series.

Further, the discussion of the relative importance of the different residues would appear to be incomplete as it is confined to the cases where ν is very large or $|\nu - z|$ is of the same or lower order than $z^{1/3}$, while the original series indicates that in general singularities of the integrand other than those for which $|\nu - z|$ is of the same or lower order than $z^{1/3}$ are effective, and these are not dealt with.

The expressions for the magnetic force at points on the surface of the sphere at a distance from the oscillator can be obtained by substituting the appropriate approximations for the Legendre functions and then summing the series as in the previous investigation or effecting the summation by the same method before the approximations are substituted. It is known* that if

$$S_m = u_n + u_{n+1} + \dots + u_{n+m-1},$$

the sum can be written

$$S_m = \frac{1}{2}(u_n - u_{n+m}) + \int_0^m u_{n+\tau} d\tau + R,$$

where R is unimportant compared with the integral when $u_{n+\tau}$ oscillates slowly with τ , whence it follows that the principal part of the sum of a converging series of this kind is given by the integral when the first term of the series can be neglected. This is the result used in the previous investigation. An expression for R as a series of integrals can be obtained which gives S_m in the form

$$S_m = \frac{1}{2}(u_n - u_{n+m}) + \int_0^m u_{n+\tau} d\tau + 2 \sum_{p=1}^{\infty} \int_0^m \cos 2p\pi\tau u_{n+\tau} d\tau, \quad (1)$$

a result which can be readily verified and which makes it possible to select the principal part of the sum of any number of terms of a series. The series for the important part of ψ is†

$$-\kappa z_0^{-2} \sum 3^{-1/3} z_0^{1/3} (2n+1) \xi^{1/3} K_{1/3}(\xi e^{-\pi i}) (1-\mu^2) \frac{dP_n}{d\mu} \Big/ \xi^{2/3} K_{2/3}(\xi e^{-\pi i}),$$

and the part arising from any one of the partial fractions whose sum expresses $\xi^{1/3} K_{1/3}(\xi e^{-\pi i}) / \xi^{2/3} K_{2/3}(\xi e^{-\pi i})$ such as $A_k / (\xi^{2/3} - n_k^{2/3} e^{5\pi i/3})$ admits of being summed completely, but to secure that terms which are not of the same order as the sum of the terms of the original series for which $|n + \frac{1}{2} - z_0|$ is of higher order than $z_0^{1/3}$ are not included, the method of summation adopted should be one which can also be applied to those terms. Applying the formula (1) to the series for ψ , since the first term of the series

* 'Phil. Trans.,' A, vol. 210, pp. 132, 133 (1909).

† 'Roy. Soc. Proc.,' A, vol. 90, p. 55 (1914).

can be neglected and the series converges, the principal part of ψ is given by the first integral when θ is not near to π , and then

$$\bar{\psi} = -\kappa z_0^{-2} \int_{-\infty}^{\infty} 3^{2/3} 6^{1/3} z_0^{2/3} (2n+1) \{ \xi^{1/3} K_{1/3}(\xi e^{-\pi i}) / \xi^{2/3} K_{2/3}(\xi e^{-\pi i}) \} \\ (1-\mu^2) \frac{dP_n}{d\mu} d\xi,$$

for $n + \frac{1}{2} = z_0 + 3 \cdot 6^{-1/3} z_0^{1/3} \zeta$,

that is, substituting Heine's expression for $P_n(\mu)$, which is given by

$$-i\pi P_n(\mu) = Q_n(\mu + 0i) - Q_n(\mu - 0i),$$

the above expression becomes

$$\bar{\psi} = \kappa z_0^{-4/3} (\pi i)^{-1} 3^{1/3} 2^{-1/3} \int_{-\infty}^{\infty} (2n+1) \{ \xi^{1/3} K_{1/3}(\xi e^{-\pi i}) / \xi^{2/3} K_{2/3}(\xi e^{-\pi i}) \} \\ (1-\mu^2) \frac{d}{d\mu} \{ Q_n(\mu + 0i) - Q_n(\mu - 0i) \} d\xi.$$

Now, as was proved in the previous investigation, all the poles of $\xi^{1/3} K_{1/3}(\xi e^{-\pi i}) / \xi^{2/3} K_{2/3}(\xi e^{-\pi i})$ are in the lower half of the ζ plane, therefore, since $Q_n(\mu - 0i)$ tends to zero at an infinite distance in the upper half of the ζ plane, when θ is not near to 0 or π , the part of the integral that depends on $Q_n(\mu - 0i)$ vanishes, and

$$\bar{\psi} = \kappa (\pi i)^{-1} z_0^{-4/3} 3^{1/3} 2^{-1/3} \int_{-\infty}^{\infty} (2n+1) \{ \xi^{1/3} K_{1/3}(\xi e^{-\pi i}) / \xi^{2/3} K_{2/3}(\xi e^{-\pi i}) \} \\ (1-\mu^2) \frac{d}{d\mu} Q_n(\mu + 0i) d\xi,$$

that is

$$\bar{\psi} = \kappa (\pi i)^{-1} z_0^{-4/3} 3^{1/3} 2^{-1/3} \int_{-\infty}^{\infty} (2n+1) \sum_{k=0}^{\infty} \{ A_k / (\xi^{2/3} - x_k^{2/3} e^{5\pi i/3}) \} \\ (1-\mu^2) \frac{d}{d\mu} Q_n(\mu + 0i) d\xi,$$

or, since $Q_n(\mu + 0i)$ tends to zero at an infinite distance in the lower half of the ζ plane, and $\xi^{2/3} = 2^{2/3} \zeta$,

$$\bar{\psi} = -\kappa z_0^{-4/3} 3^{-1/3} \sum_{k=0}^{\infty} (2n_k+1) A_k (1-\mu^2) \frac{d}{d\mu} Q_{n_k}(\mu + 0i),$$

where

$$n_k + \frac{1}{2} = z_0 + \frac{1}{2} (3x_k)^{2/3} z_0^{1/3} e^{5\pi i/3}, \quad A_k = 2x_k^{1/3} (3x_k)^{-1} e^{-5\pi i/3},$$

therefore

$$\bar{\psi} = -4\kappa z_0^{-4/3} \sum_{k=0}^{\infty} (n_k + \frac{1}{2}) (3x_k)^{-2/3} e^{-5\pi i/3} (1-\mu^2) \frac{d}{d\mu} Q_{n_k}(\mu + 0i), \quad (2)$$

when θ is not near to 0 or π . When $\sin \frac{1}{2} \theta$ is a small quantity, $Q_n(\mu + 0i)$ can be replaced by $K_0 \{ i(2n+1) \sin \frac{1}{2} \theta \}$, and the expression for $\bar{\psi}$ becomes

$$\bar{\psi} = -4\kappa i z_0^{-4/3} e^{-5\pi i/3} \sin \theta \cos \frac{1}{2} \theta \sum_{k=0}^{\infty} (n_k + \frac{1}{2})^2 (3x_k)^{-2/3} K_1 \{ i(2n_k+1) \sin \frac{1}{2} \theta \},$$

or substituting the asymptotic value for K_1 and, retaining the principal parts only

$$\overline{\psi} = -4\kappa\iota\pi^{1/2} (z_0^{1/3} \sin \frac{1}{2}\theta)^{1/2} \cos^2 \frac{1}{2}\theta e^{-2iz_0 \sin \frac{1}{2}\theta + \pi\iota/12} \sum_{k=0}^{\infty} (3\alpha'_k)^{-2/3} e^{-(3\alpha_k)^{2/3} \pi\iota/6} z_0^{1/3} \sin \frac{1}{2}\theta. \quad (3)$$

The preceding analysis is identical with that of the previous investigation,* except that the approximation for the Legendre function has been substituted after the summation has been effected, and the result (3) is the same.

When $\sin \frac{1}{2}\theta$ is not small, the appropriate approximation for $Q_n(\mu + 0\iota)$ is given by

$$Q_n(\mu + 0\iota) = \pi^{\frac{1}{2}} (2n \sin \theta)^{-\frac{1}{2}} e^{-(n+\frac{1}{2})\theta\iota - \frac{1}{2}\pi\iota},$$

and the corresponding expression for $\overline{\psi}$ becomes

$$\overline{\psi} = -4\kappa\iota\pi^{1/2} (\frac{1}{2}z_0^{1/3} \sin \theta)^{1/2} e^{-iz_0\theta + \pi\iota/12} \sum_{k=0}^{\infty} (3\alpha_k)^{-2/3} e^{-1/2(3\alpha_k)^{2/3} \pi\iota/6} z_0^{1/3} \sin \theta. \quad (4)$$

It is readily verified that, for the larger values of θ , for which the ratio $\overline{\psi}/\overline{\psi}_1$ is sensible for the wave-lengths in use in wireless telegraphy, the difference between the expressions (3) and (4) is insensible.†

As θ approaches π , the rate of oscillation of the terms in the series increases and approaches that of $\cos n\pi$, and the appropriate expression‡ for $P_n(\mu)$ is $\cos n\pi P_n(\mu')$, where $\mu' = \cos(\pi - \theta) = -\mu$.

If, in the series for S_m , $u_n = v_n \cos n\pi$, the formula (1) becomes

$$S_m = \frac{1}{2}(u_n - u_{n+m}) + \int_0^m v_{n+\tau} \cos(n+\tau)\pi d\tau \\ + 2 \sum_{p=1}^{\infty} \int_0^m v_{n+\tau} \cos(n+\tau)\pi \cos 2p\pi\tau d\tau,$$

that is

$$S_m = \frac{1}{2}(u_n - u_{n+m}) + \cos n\pi \int_0^m v_{n+\tau} \cos \tau\pi d\tau \\ + \cos n\pi \sum_{p=1}^{\infty} \int_0^m v_{n+\tau} \{ \cos(2p+1)\tau\pi + \cos(2p-1)\tau\pi \} d\tau,$$

$$\text{or} \quad S_m = \frac{1}{2}(u_n - u_{n+m}) + 2 \cos n\pi \sum_{p=0}^{\infty} \int_0^m v_{n+\tau} \cos(2p+1)\tau\pi d\tau,$$

and the principal part of the sum of the series, when $v_{n+\tau}$ is oscillating slowly with τ , and the first and last terms can be neglected, is

$$2 \int_0^m v_{n+\tau} \cos \tau\pi d\tau \cos n\pi.$$

* 'Roy. Soc. Proc.,' A, vol. 90, p. 56 (1914).

† The necessary comparison was made when the previous paper was written, but the result appeared to be sufficiently obvious without writing out the analysis.

‡ 'Phil. Trans.,' A, vol. 210, p. 120 (1909).

Hence, when θ is approaching π , the principal part of

$$-\kappa z_0^{-2} 3^{-1/3} z_0^{1/3} \sum (2n+1) \{ \xi^{1/3} K_{1/3}(\xi e^{-\pi i}) / \xi^{2/3} K_{2/3}(\xi e^{-\pi i}) \} (1-\mu^2) \frac{dP_n}{d\mu}$$

is given by

$$\bar{\Psi} = 2\kappa z_0^{-2} 3^{1/3} 2^{-1/3} z_0^{1/3} \int_{-\infty}^{\infty} \{ (2n+1) \xi^{1/3} K_{1/3}(\xi e^{-\pi i}) / \xi^{2/3} K_{2/3}(\xi e^{-\pi i}) \} (1-\mu^2) \frac{dP_n}{d\mu} \cos n\pi d\xi,$$

where

$$n + \frac{1}{2} = z_0 + 3 \cdot 6^{-1/3} z_0^{1/3} \xi;$$

now $e^{n\pi i} Q_n(\mu' + 0i)$ and $e^{n\pi i} Q_n(\mu' - 0i)$ both tend to zero at an infinite distance in the upper half of the ξ plane, therefore

$$\bar{\Psi} = \kappa z_0^{-2} 3^{1/3} 2^{-1/3} z_0^{1/3} \int_{-\infty}^{\infty} (2n+1) \{ \xi^{1/3} K_{1/3}(\xi e^{-\pi i}) / \xi^{2/3} K_{2/3}(\xi e^{-\pi i}) \} (1-\mu'^2) \frac{dP_n}{d\mu'} e^{-n\pi i} d\xi.$$

Again $e^{-n\pi i} Q_n(\mu' + 0i)$ and $e^{-n\pi i} Q_n(\mu' - 0i)$ both tend to zero at an infinite distance in the lower half of the ξ plane, therefore

$$\bar{\Psi} = \kappa z_0^{-4/3} 3^{1/3} \sum_{k=0}^{\infty} 2x_k^{1/3} (3x_k)^{-1} e^{-5\pi i/3} (2n_k+1) e^{-n_k\pi i} (1-\mu'^2) \frac{d}{d\mu'} \{ Q_n(\mu' + 0i) - Q_n(\mu' - 0i) \}.$$

When $\sin \frac{1}{2} \theta'$ is not small this becomes

$$\bar{\Psi} = -4\kappa i \pi^{1/2} (\frac{1}{2} z_0^{1/3} \sin \theta')^{1/2} \left[e^{-z_0(\pi-\theta')} i + \pi i/12 \sum_{k=0}^{\infty} (3x_k)^{-2/3} e^{-1/2(3x_k)^{2/3} z_0^{1/3} e^{\pi i/6} (\pi-\theta')} + e^{-z_0(\pi+\theta')} i - \pi i/12 \sum_{k=0}^{\infty} (3x_k)^{-2/3} e^{-1/2(3x_k)^{2/3} z_0^{1/3} e^{\pi i/6} (\pi+\theta')} \right]. \quad (5)$$

When $\sin \frac{1}{2} \theta'$ is small, the expression for $\bar{\Psi}$ becomes, after substitution of the appropriate approximations for the spherical harmonics in terms of the Bessel functions,

$$\bar{\Psi} = -8\kappa i \pi^{1/2} (z_0^{1/3} \sin \frac{1}{2} \theta')^{1/2} \cos^2 \frac{1}{2} \theta' \sum_{k=0}^{\infty} (3x_k)^{-2/3} e^{-5\pi i/3} e^{-n_k\pi i} [\cos(2n_k+1) \sin \frac{1}{2} \theta' - \frac{3}{4}\pi],$$

that is

$$\bar{\Psi} = -4\kappa i \pi^{1/2} (z_0^{1/3} \sin \frac{1}{2} \theta')^{1/2} \cos^2 \frac{1}{2} \theta' \left[e^{-z_0(\pi-2 \sin \frac{1}{2} \theta')} i + \pi i/12 \sum_{k=0}^{\infty} (3x_k)^{-2/3} e^{-1/2(3x_k)^{2/3} z_0^{1/3} e^{\pi i/6} (\pi-2 \sin \frac{1}{2} \theta')} + e^{-z_0(\pi+2 \sin \frac{1}{2} \theta')} i - \pi i/12 \sum_{k=0}^{\infty} (3x_k)^{-2/3} e^{-1/2(3x_k)^{2/3} z_0^{1/3} e^{\pi i/6} (\pi+2 \sin \frac{1}{2} \theta')} \right]. \quad (6)$$

As in the previous investigation,* it can be shown that the inclusion of

* *Loc. cit.*, p. 57.

terms for which $|n + \frac{1}{2} - z|$ is of higher order than $z_0^{1/3}$, does not affect the results (5) and (6).

As ψ vanishes when $\theta = \pi$, whereas the electric force normal to the surface does not vanish, it is convenient to obtain the value of E_r when θ is equal to or in the neighbourhood of π . Now

$$E_r = i\kappa V z_0^{-2} \frac{\partial \psi}{\partial \mu},$$

whence the principal part of E_r is given by

$$\bar{E}_r = 4\kappa^2 \pi V z_0^{-10/3} \sum_{k=0}^{\infty} (3x_k)^{-2/3} e^{-5\pi i/3} (n_k + \frac{1}{2})^3 e^{-n_k \pi i} J_0 \{ (2n_k + 1) \sin \frac{1}{2} \theta' \},$$

that is

$$\bar{E}_r = -4\kappa^2 \pi V z_0^{-1/3} e^{-\pi i z_0 - \pi i/6} \sum_{k=0}^{\infty} (3x_k)^{-2/3} e^{-1/2 (3x_k)^{2/3} \pi z_0^{1/3} e^{\pi i/6}} J_0 \{ 2z_0 \sin \frac{1}{2} \theta' + (3x_k)^{2/3} z_0^{1/3} e^{5\pi i/3} \sin \frac{1}{2} \theta' \}. \quad (7)$$

When $\theta = \pi$, that is when $\theta' = 0$, this becomes

$$\bar{E}_r = -4\kappa^2 \pi V z_0^{-1/3} e^{-\pi i z_0 - \pi i/6} \sum_{k=0}^{\infty} (3x_k)^{-2/3} e^{-1/2 (3x_k)^{2/3} \pi z_0^{1/3} e^{\pi i/6}},$$

and the important part of this is

$$\bar{E}_r = -4\kappa^2 \pi V z_0^{-1/3} e^{-\pi i z_0 - \pi i/6} (3x_0)^{-2/3} e^{-1/2 (3x_0)^{2/3} \pi z_0^{1/3} e^{\pi i/6}},$$

which, for the wave-lengths in use in wireless telegraphy, is insensible. Formula (7), in the neighbourhood of $\theta' = 0$, can be treated on similar lines to the corresponding formula for the bright point in the shadow behind an object. It should be observed that, in the above method, there is no special difficulty connected with the point $\theta = \pi$.

The formula (3) represents the effect for all distances at which the effect is sensible for the wave-lengths in use, and, as was shown in the former investigation, tends to the value $2\bar{\mathcal{T}}_1$ as the oscillator is approached; the formula (4) represents the effect for greater distances, until the angular distance is approaching π , when the appropriate formula is (5), when $\pi - \theta$ is not small, and (6) when $\pi - \theta$ is small. Formula (7) gives the electric force at the point $\theta = \pi$ and in the neighbourhood.

Forces in Surface Films. Part I.—*Theoretical Considerations.*
 Part II.—*Experimental Observations and Calculations.*
 Part III.—*The Charge on Colloids.*

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PART I.

In an earlier paper* on the adsorption of vapours, the author was led to make the assumption that the specific volume of the last portion of fluid adsorbed from the saturated vapour phase was the same as the specific volume of the liquid in equilibrium with the vapour. This led to a consideration of the nature of the surface film, and certain consequences of the variation in density there from the density of the liquid in bulk were immediately obvious, and are discussed below. Experimental proof of one of these was easily obtained by the author, and, recently, certain other observers, approaching the subject from a different aspect, have published evidence† with a promise of further work.

Let us consider the determination of the density of a finely divided solid by the usual immersion method, assuming that all gases such as air have been removed from the solid and the pure liquid. Let us assume that upon the surface of the solid there is a film amounting to α grm. liquid per gramme solid where the mean specific volume of the liquid is v_2 instead of v_1 , the value for the liquid in bulk. If the true specific volume of the solid is v , and v_0 is the volume ordinarily observed and calculated without regard to α , then, from a consideration of the total volume occupied by a gramme of the solid and the accompanying film, we see that

$$v + \alpha v_2 = v_0 + \alpha v_1$$

and $\therefore$

$$v = v_0 + \alpha (v_1 - v_2). \quad (1)$$

The second term on the right-hand side of (1) will only assume importance in the case of substances with a very large specific surface, and here, owing to the different compressibilities of various liquids, it seems reasonable to

* 'Trans. Faraday Soc.,' vol. 10, p. 167 (1914).

† Cude and Hulett, 'Jour. Amer. Chem. Soc.,' vol. 42, p. 391 (1920).

expect $\alpha(v_1 - v_2)$ to vary from liquid to liquid, and hence v_0 to vary from liquid to liquid. This, in fact, has been observed by the author and others.

There is a second source of variation of v_0 , for the surface may not be equally accessible to molecules of different liquids. Thus there may be a portion of the surface accessible to a water molecule (van der Waals' $b = 14 \times 10^{-4}$), but not accessible to a chloroform molecule ($b = 45 \times 10^{-4}$). We may therefore regard v as the space embraced by 1 gm. of the solid and not occupied by the liquid molecules when immersed in the liquid of greatest penetrating power, which for all practical purposes is water. We may conceive of a particle of the solid as possessing regions h, h, h , which are holes not accessible even to water molecules or ions, while another hole, k , is accessible to water but not to chloroform. Hence v includes the portions of space h, h, h , and, for water, equation (1) holds. On the other hand, if we denote the volume of the portions k by the symbol Δv , the equation for chloroform is

$$v + \Delta v' = v_0' + \alpha'(v_1' - v_2'), \quad (2)$$

where the dashes refer the various quantities to chloroform. Hence with a substance of surface not equally accessible to different liquids, we should be able to group determinations of the specific volume according to varying values of Δv , if we could determine the quantities on the right-hand side of (2). This grouping will presumably follow the order of molecular size.

Let us now assume we are dealing with a group of liquids for which the accessible surface of the solid under examination is the same. From equation (2), if we graph v_0 against $\alpha(v_1 - v_2)$ we will obtain a straight line whose intercept on the v_0 axis is $v + \Delta v$. But the value of $\alpha(v_1 - v_2)$ is not ordinarily known, for while α may be determined from observations on adsorption from the vapour phase and v_1 is known, v_2 remains undetermined save from theoretical considerations. If we could select a function of $\alpha(v_1 - v_2)$, we would obtain a curve giving the required intercept on plotting such a function against v_0 , but there is no obvious function available. On the other hand, it seems reasonable to assume that the less compressible a liquid is the smaller the value of $\alpha(v_1 - v_2)$. Thus for an incompressible liquid $v_1 = v_2$, and here, therefore, $v_0 = v + \Delta v$. Hence, if we could obtain observations on a sufficient number of liquids with different compressibilities, it should be possible to extrapolate to a value of $v + \Delta v$ from the (β, v_0) curve. Once this value was obtained equation (2) would give us $\alpha(v_1 - v_2)$ and if α and v_1 were known v_2 would be known, and hence also the compressive (or distensive) force

acting on the interfacial film. Denoting by p the pressure which changes v_1 to v_2 , and by β the mean compressibility of the liquid for the range of pressure considered we have

$$v_1 - v_2 = pv_1\beta$$

and $\therefore$

$$v + \Delta v = v_0 + \alpha pv_1\beta. \quad (3)$$

Since β varies somewhat with p , it is evidently desirable to have an estimate of the magnitude of p (which again may vary from liquid to liquid) before we can select the values of the compressibility to be used as indicated above, and so recourse must be made to theoretical considerations.

The author has previously* identified the compressive force in question with those giving rise to cohesion in liquids and represented by the term a/v^2 in van der Waals' equation,

$$(p + a/v^2)(v - b) = RT.$$

Since the attraction of a liquid for itself is represented approximately by the expression a/v^2 or $a^{1/2}/v \times a^{1/2}/v$ we may assume that the attraction between the solid and the liquid in the film is approximately represented by $a_0^{1/2}/v \times a^{1/2}/v_2$ where a_0 and v refer to the solid and a and v_2 to the liquid. This is the attraction per unit area across the interface solid-liquid. We may now conceive two cases to arise according as the adsorbed fluid is almost entirely surrounded by the adsorbent, that is, in capillary tubes or is only bounded on one side by the adsorbent. In the first case it is easy to conceive of the whole adsorbed fluid as being under the cohesive attraction of the adsorbent provided the capillaries are sufficiently small. In the second case the compression will be very great in the molecular layer next the adsorbent and fall rapidly to zero within a few layers. We may, therefore, for purposes of calculation assume the interfacial film in this case to be in two parts, one half being highly compressed under the influence of the adsorbent while the compression in the other half under attraction of the liquid is relatively small. In the first case we assume that the total amount adsorbed α is compressed, in the second case that only $\frac{1}{2}\alpha$ is compressed. It is obvious that these assumptions could be made with regard to the calculations based on the graphical method suggested in the preceding paragraph, and in any case the first assumption will lead to a smaller estimate of the mean compressive force acting on the adsorbate, since a greater volume is compressed. This assumption we will adopt, taking the whole fluid in the adsorption layer as of specific volume v_2 , under an attractive force $a_0^{1/2}/v \times a^{1/2}/v_2$. This force will function, both as an external pressure

* 'Roy. Soc. Proc.,' vol. 96, A, p. 287 (1919).

and as an "internal" pressure so that the fluid in the film will be as if under an external force p such that

$$p + a/v_2^2 = a_0^{\frac{1}{3}}/v \times a^{\frac{1}{3}}/v_2. \quad (4)$$

Equation (4) may also be derived by considering that the pull inwards of the adsorbent will be opposed by the internal cohesion of the film itself leaving an excess p to function as a pressure. From (4) we derive an expression for p as

$$p = a^{\frac{1}{3}}/v_2 (a_0^{\frac{1}{3}}/v - a^{\frac{1}{3}}/v_2), \quad (5)$$

and an expression for $a_0^{\frac{1}{3}}/v$ as

$$a_0^{\frac{1}{3}}/v = (p + a/v_2^2)/a^{\frac{1}{3}}/v_2. \quad (6)$$

Since observations on the compression of a liquid give us the relation between p and v_2 , if we determine one of these we can further determine a_0/v^2 or the "internal" pressure of the adsorbent.

PART II.

Determination of v_0 .

The substance selected as possessing a surface large enough to give the effect sought for was blood charcoal. Some highly purified material was dried in an oven at 120° C. and subsequently transferred to a desiccator over phosphorus pentoxide where it was kept several weeks. The specific volume was determined by the usual method employed in the case of powders using a silica specific gravity bottle of approximately 50 c.c. Two liquids were employed, water and chloroform. About 2 grms. of the charcoal were rapidly weighed in the specific gravity bottle and then covered with the liquid. The bottle was now placed in a bath of the liquid and the temperature raised to the boiling point with careful stirring, and kept there for several hours. The bottle was then completely filled with the freshly boiled liquid and the stopper inserted at a marked position. The stopper had a cup-shaped top in which was placed excess of the liquid to allow for contraction and evaporation during immersion in the thermostat. After sufficient immersion the meniscus was adjusted, the cup stoppered, and the bottle removed, cooled to weighing-room temperature, dried, and subsequently weighed. It was found possible by this simple method* to obtain readings with chloroform alone at 25° C., whose variation from the mean was not more than 1 mgrm., corresponding to an error of 0.01° in the thermostat temperature. In the subsequent calculations the weight of the charcoal was corrected for the

* These experiments were made in 1919 before the publication of the paper by Cude and Hulett. They were first attempted in 1916 with a glass s.g. bottle.

adsorbed gases which were present when it was weighed, and which were expelled on immersion in the liquid. The values of v_0 thus obtained were consistent within 0.2 per cent. A specimen determination and calculation is given below in Table I, where ic is the correction for adsorbed gases, and

Table I.

Duration of boiling.....	3 hours.	6 hours.	10 hours.	13 hours.
Temperature of thermostat	25°·02 C.	24°·88 C.	24°·95 C.	24°·94 C.
Mass in air of CHCl_3	74·097	74·111	74·104	74·105
" " charcoal	1·877	1·877	1·877	1·877
" " CHCl_3 and charcoal	75·974	75·988	75·981	75·982
$\Delta\text{CHCl}_3 + ic$	74·660	74·677	74·675	74·672
ic	1·314	1·311	1·306	1·310
c	0·085	0·085	0·085	0·085
ΔCHCl_3	1·792	1·792	1·792	1·792
Volume of CHCl_3	1·229	1·226	1·221	1·225
Spec. vol. of charcoal	0·830	0·828	0·825	0·827
	0·463	0·462	0·460	0·462

ΔCHCl_3 the mass in air of the chloroform apparently displaced by the evacuated charcoal, c . It will be seen that after several hours' boiling, consistent results were obtained. The chloroform was the purest B.P. chloroform, which was found free from charring on shaking with concentrated sulphuric acid. It was shaken up with water to dissolve out alcohol and then treated with fused calcium chloride, to remove water, and subsequently with fused caustic potash, to destroy carbonyl chloride, etc., decanted, and distilled. On fractional distillation practically the whole preparation passed over between 61.4°–61.5° at 76.4 cm. pressure. Three determinations of the chloroform in the s.g. bottle (50.095 c.c.) at 25° C. gave 74.149, 74.149, and 74.147 grm., corrected to vacuo. The mean value gave a density of 1.48016 grm. per cubic centimetre at 25° C., while a second preparation gave 1.48007. After decantation from the charcoal the density of the first preparation was found to be 1.48010 (one determination). The divergence is within the limits of errors of observation and there is no evidence of anything being imparted to, or withdrawn from, the chloroform upon contact with the adsorbent. It may be mentioned that the density at 25°, as determined by Thorpe was 1.4791, while Pierre gives 1.4803.

The values of v_0 for water were found to be 0.510 and 0.512 at 25° C., and 0.518 and 0.519 at 40° C., while for chloroform the values were 0.460 and 0.461 at 25° C. Thus at 25° C. the mean values were 0.511 and 0.461, a

divergence well outside any possible experimental error. It may here be pointed out that any error in the correction for gases adsorbed and subsequently expelled would alter the values in practically the same proportion.

We may compare these results with those obtained by Cude and Hulett (*loc. cit.*) from their less finely divided charcoal. This is done in Tables III and IV. Here the last column gives the compression at 20° C. of the given

Table III (Williams).

Liquid.	v_0 .	b .	$p\beta$.
H ₂ O	0·511	14×10^{-4}	0·020
CHCl ₃	0·461	45	0·036

Table IV (Cude and Hulett).

Liquid.	v_0 .	b .	$p\beta$.
H ₂ O	0·539	14×10^{-4}	0·020
CS ₂	0·504	34	0·036
C ₆ H ₆	0·556	54	0·034
CCl ₄	0·607	57	0·038

liquid under a pressure of 500 atmospheres. The data are taken from Bridgman* and from Richards.† It will be seen that in the case of Table III the compressibility appears to be a chief factor determinating the value of v_0 , while in Table IV the determinations fall into two groups according as b is greater or less than, say, 40×10^{-4} , that is, while we may assume that the charcoal used by the present author had a surface equally accessible to water and chloroform molecules, this assumption could scarcely be made for the other specimen and liquids employed. This is in accordance with the theory developed in Part I. It may also be pointed out that benzene‡ freezes at 25° C. under a pressure of about 670 atmospheres with a change in volume of 0·11 c.c. per gramme while carbon tetrachloride at 25° C. freezes under about 1,400 atmospheres with a change in volume of only 0·02 c.c. per gramme. This may not be unconnected with the variation of v_0 observed, which is certainly in the required direction, the compression of the benzene under suitable pressure being greater than that of the carbon tetrachloride.

It is obvious that if the surface of the first charcoal was not so accessible to

* 'Proc. Amer. Acad. Arts and Sc.,' vol. 47, p. 411 (1912); vol. 49, p. 1 (1913).

† Richards, Stull, Mathews, and Speyers, 'Jour. Amer. Chem. Soc.,' vol. 34, p. 988 (1912).

‡ Bridgman, 'Phys. Rev.' (2), vol. 3, pp. 126, 153 (1914).

the chloroform as to the water, an increase in the accessibility to the chloroform would *reduce* the corresponding v_0 value both because more space would be occupied by the chloroform and because the extra chloroform would be compressed. (We are not considering such a splitting up as would sensibly reduce the cohesive forces of the adsorbent.) A correction thus introduced would lower the value of the right-hand side of (7) below and reduce to some extent the estimate of the cohesive forces.

Determination of α and Calculation of the Surface Cohesion.

Several years ago* the author made a series of observations on the mass of vapour picked up at 25° C. by 1 gram. of evacuated charcoal from the saturated vapour of different liquids. He was unable to detect any regularity in the results, such as, for example, that of equal volumes found by Bachmann† with silica and by Gurvich‡ with fuller's earth which led these authors and Langmuir§ to conclude that the approximately equal volumes represented the volume of capillary pores of the adsorbent. Because of the lack of any simple relation among the values found, the experiments were never published, but the determinations on water and chloroform have now proved useful. The charcoal was evacuated at 100° C. by a Töpler pump, *i.e.*, under conditions comparable with the boiling out underneath the liquid in the later experiments. After making all corrections, the mean of two closely concordant observations at 25° C. gave for water 0.75 gram. and for chloroform 1.26 gram. Hence the volume of the water adsorbed was 0.75 c.c. and of the chloroform 0.85 c.c. These volumes are not equal, nor apparently are the volumes under compression on the adsorbent, for then we would have

$$v_0 + \alpha v_1 = v_0' + \alpha' v_1',$$

which is not true. Instead we have the equations

$$\begin{aligned} v &= 0.511 + 0.75(1 - v_2/v_1), \\ &= 0.461 + 0.85(1 - v_2'/v_1'), \end{aligned}$$

whence

$$0.85 v_2'/v_1' - 0.75 v_2/v_1 = 0.5. \quad (7)$$

Knowing the variation in volume of water and chloroform under pressure, we can tabulate pressures which fulfil condition (7). The variation in volume is presented in Table V, where it has been assumed that the film of

* Liverpool, 1912-13. The author wishes to acknowledge here his indebtedness to Prof. F. G. Donnan, F.R.S., for his encouragement and advice in the execution of these apparently profitless experiments.

† 'Z. f. Anorg. Chem.,' vol. 79, p. 202 (1912).

‡ 'J. Russ. Phys. Chem. Soc.,' vol. 47, p. 805 (1915).

§ 'J. Amer. Chem. Soc.,' vol. 39, p. 1848 (1917).

Table V.

Pressure.	Relative volume.			
Hgrm./Cm. ²	Water.		Chloroform.	
1	1.00	0.75	1.00	0.85
1,000	0.96	0.72	0.93	0.79
3,000	0.91	0.68	0.86	0.73
5,000	0.87	0.65	0.82	0.70
7,000	0.84	0.63	0.79	0.67
9,000	0.81	0.61	0.77	0.65
11,000	0.80	0.60	0.75	0.64

chloroform did not freeze, and that its compressibility was closely the same as that of isobutyl alcohol.* In Table VI are then given the pressures satisfying equation (7). Corresponding to these pressures, we may evaluate $a_0^{\frac{1}{2}}/v$ by means of equation (6), and find when the two values from the two liquids coincide. This evaluation is given in Table VII, where the values of "a" for chloroform and for water have been taken as 2930×10^{-5} and 1089×10^{-5} respectively, leading to cohesions at atmospheric pressure and 25° C. of 2300 kgrm./cm.² and 17,300 kgrm./cm.²

Table VI.

CHCl ₃ .		H ₂ O.	
p.	$p + a/v_2^2$.	p.	$p + a/v_2^2$.
1,000	3,700	300	18,000
7,000	10,700	8,000	33,000
9,000	12,900	10,000	37,000
10,000	13,900	11,000	38,000
11,000	15,000	12,000	40,000

Table VII.

$a_0^{\frac{1}{2}}/v$.	
CHCl ₃ .	H ₂ O.
0.7×10^2	1.3×10^2
1.8	2.1
2.1	2.2
2.2	2.3
2.4	2.4

From Table VII, we see that the required coincidence in the $a_0^{\frac{1}{2}}/v$ values only occurs when the chloroform and water are under pressures of 11,000 kgrm. and 12,000 kgrm. per cm.² respectively.

Now, chloroform in bulk freezes at 25° C. under 5500 kgrm. pressure and water at 9800 kgrm. (Bridgman). If solidification takes place in the adsorption layer, the effect would be a diminution of the volume of the chloroform of 0.045 c.c. per gramme, which would push the corresponding pressure for

* In a private communication to the author, P. W. Bridgman states that the compressibility at 40° was practically the same as that of isobutyl alcohol. The author desires to acknowledge his indebtedness for this information.

water above 10,000 kgrm., that is, the order of magnitude of the compressive forces is not affected.* Keeping, however, to our assumption of a liquid film, we see that the compression in the chloroform is from 0.85 c.c. to 0.64 c.c., or 0.21 c.c. in all, whence the specific volume of the charcoal is not 0.46 but $0.46 + 0.21$, or 0.67 c.c. The water observation naturally leads to the same result.

We also have at our disposal an estimate of the internal cohesion of the charcoal. To satisfy equation (7) and equation (6) for the two liquids, $a_0^{\frac{1}{3}}/v$ had to be 2.4×10^2 , whence a_0/v^2 is 58,000 kgrm. per cm.², an internal pressure three times that of water at ordinary temperatures and pressures.

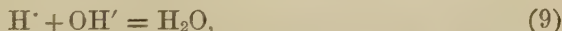
PART III.

Having obtained an estimate of the compressive force in an adsorption layer it is of interest to examine some consequences of the existence of a force of this magnitude. Lagergren†, assuming the force to be of the order of 10,000 atmospheres—curiously enough the same estimate as that found in Part II above—calculated the effect on the solubility of different salts in aqueous solution and correlated it with the positive or negative adsorption he found for them with kaolin and charcoal. We will, however, confine our attention to the case of a finely divided substance in suspension in pure water, and examine the effect on the dissociation of the water (assumed liquid) in the adsorption layer.

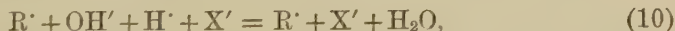
The effect of pressure on a chemical reaction in solution has been investigated thermodynamically by Planck‡ who deduced the relation.

$$\frac{d \log K}{dP} = \frac{V_1 - V_2}{RT}, \quad (8)$$

where K is the equilibrium constant, P the pressure and $V_1 - V_2$, the volume change during the reaction. The reaction here considered is:—



where the total volume change may be estimated from the volume change in a reaction of the type



* Such solidification, if it exists, could be detected by dilatometric measurements which would thus furnish an independent estimate of the pressure from the temperature determination. We are not dealing with liquid in wide capillaries such as is found in some silica gels and lamp black, upon which observations of this nature have been made. See Foote and Saxton, 'Journ. Amer. Chem. Soc.', vol. 39, p. 627, etc. (1917).

† 'Bihang till K. Svenska Vet. Akad. Handl.', vol. 24, II, p. 4 (1898).

‡ 'Thermodynamics,' 1903, equation (220). See also Williams, 'Trans. Faraday Soc.' (in the press).

that is, the neutralization of a strong base by a strong acid in dilute solution. Ostwald* found the neutralisation of normal solutions of strong acids by strong bases led to an increase in volume of approximately 20 cc. By far the greater part of this increase is due to the reaction in equation (9). By extrapolating to infinite dilution for the molar volumes of a few acids, bases, and salts given in Landolt-Börnstein the author found that the change of volume involved lay between 18 and 22 cc., in agreement with Ostwald's direct determination. We may therefore take 20 cc. as the value of $V_1 - V_2$ in equation (9) and calculate the value of the right-hand side. We have

$$\frac{d \log K}{dP} = \frac{V_1 - V_2}{RT} = \frac{20 \times 273}{22400 \times 298}$$

or
$$\frac{d \log_{10} K}{dP} = \frac{20 \times 273}{2.3 \times 22400 \times 298} = 0.0036,$$

when P is expressed in atmospheres. Integrating on the assumption that $V_1 - V_2$ is appreciably constant we have approximately

$$\log_{10} K_2 - \log_{10} K_1 = 0.0036 (P_2 - P_1)$$

so that when P_2 is 12,000 atmospheres we have

$$\log_{10} K_{12000} = \log_{10} K_1 + 4.3 = 14.0 + 4.3 = 18.3,$$

whence the concentration of H' and OH' is 10^{-5} in the adsorption layer as against 10^{-7} in the water outside.

We may expect as a result of this increased concentration of ions in the adsorption layer that a diffusion potential will be set up of the same type as has been investigated by Nernst, who gives for the diffusion potential difference between two solutions of ionic concentrations c_1 and c_2 respectively the well-known formula

$$E = \frac{RT}{n} \frac{u-v}{u+v} \log c_1/c_2.$$

Assuming that u and v are equally affected by the compression this formula becomes at 25° C. for H' and OH' .

$$\begin{aligned} E &= 0.016 \times \log_{10} c_1/c_2 = -0.016 \times \frac{1}{2} \log_{10} K_{12000}/K_1 \\ &= -0.16 \times \frac{1}{2} \times 4.3 = -0.034 \text{ volts,} \end{aligned}$$

that is, the adsorption layer will have a potential 0.034 volts lower than the surrounding fluid, and the charcoal particle will thus appear to be negatively charged when immersed in pure water. The order of magnitude of this calculated potential difference agrees with observations made on particles suspended in water. Since graphite appears negatively charged,† a negative

* 'J. Prakt. Ch.' (2), vol. 18, p. 353 (1878).

† Burton, 'Physical Properties of Colloidal Solutions,' p. 125.

sign is to be expected for charcoal particles. We, therefore, see that the existence in the adsorption layer of compressive forces of the magnitude given is sufficient to explain in sign and magnitude the potential differences and apparent charge on certain particles suspended in fluids.

From the simple theory outlined above we should expect that substances with a cohesion larger than water would appear negatively charged when immersed in it, while those with a smaller cohesion would appear positively charged. The positive ion of water moves faster than the negative ion, and we should have the reverse order of apparent change in a fluid giving rise to ions where the negative ion moves faster than the positive ion.

Confining our attention again to pure water, we see that, in order to give rise to an apparent positive change, the adsorption film must be not compressed, but distended. Even allowing an extremely small internal cohesion for any substance in suspension, it seems improbable that the magnitude of the distensive forces can be as great as those of the cohesive forces, and hence we would expect any observed positive potential differences to be less in magnitude than negative P.Ds. (ignoring "dilution" of the water). This is, however, not the case* and we therefore must look for some further source of P.D. Again, chloroform and various oil emulsions† have been reported as possessing negative changes, although the internal cohesions of chloroform and some oils are certainly less than the internal pressure of water. Since the concentrations of hydrogen and hydroxyl ions necessary to give rise to the observed P.D. are extremely small, very small concentrations indeed of an electrolyte would superimpose other electrical diffusion effects and so alter the magnitude and even the sign of the P.D. arising from the cohesive forces in the adsorption layer. Thus in the case of chloroform mentioned above any reaction in the adsorption layer giving rise to hydrochloric acid even to a very small extent would cause the chloroform particles to appear *negatively* charged, as is found, through the increased concentration of the hydrogen ions. In the same way instead of attributing a very small cohesion to ferric hydroxide sol, we might expect it to give rise to hydroxyl ions as well as some relatively immobile positive ions so that it appears positively charged.‡

We have now briefly discussed the theory that the origin of the apparent charge in colloids and suspensions lies in a diffusion potential difference arising from ions produced either by the action of cohesive forces on the adsorption layer or from ionisation direct or indirect of the dispersoid. It

* Burton, *loc. cit.*, p. 135.

† Burton, *loc. cit.*, p. 126.

‡ Compare also Duclaux, 'Jour. Chim. Phys.', vol. 5, p. 29 (1907).

seems of interest to examine very briefly the effect of the presence of electrolytes in the dispersion medium.

In the theory outlined above the sign of the P.D. is attributed to the tendency to diffusion away from the adsorption layer of excess of either fast moving hydrogen or hydroxyl ions. Thus with a negative colloid there is a greater concentration of H⁺ in the adsorption layer than in the rest of the dispersion medium. Now, as is well known, Linder and Picton* found on precipitating arsenious sulphide, a negative colloid, with barium chloride, that the supernatant liquid was acid. It is obvious that preferential adsorption of the basic portion of the products of hydrolysis of a normal salt would leave outside the adsorption layer sufficient hydrogen ions to neutralise the effect of the hydrogen ions in the adsorption layer and so reduce or destroy the original potential difference with consequent precipitation of the colloid.

Summary of Parts I, II and III.

(1) Attention is directed to the effects of (i) accessibility of surface, and (ii) adsorption, on the apparent specific volume of finely divided solids.

(2) Observations are in agreement with the simple theory of these effects.

(3) The true specific volume of a specimen of charcoal which appeared to be 0.51 in water and 0.46 in chloroform, was evaluated as 0.67 c.c. per gramme.

(4) The attractive pressure in the surface film on the charcoal was calculated to be of the order of 10,000 atmospheres, while the internal pressure of the charcoal itself was estimated as of the order of 50,000 atmospheres.

(5) It is shown that such compressive forces may give rise in the adsorption layer to a diffusion potential difference of the magnitude observed in the case of suspensoids.

* 'Jour. Chem. Soc.,' vol. 67, p. 63 (1895), and vol. 87, p. 1906 (1905). See also Whitney and Ober, 'Jour. Amer. Chem. Soc.,' vol. 23, p. 842 (1901).

The Relationship between Pressure and Temperature at the Same Level in the Free Atmosphere.

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An important set of correlation coefficients showing the relationship between pressure and temperature at the same level in the free atmosphere has recently been published by W. H. Dines.* The coefficients are reproduced here in Table I.

Table I.—Correlation Coefficients between Pressure and Temperature at the same Level in the Free Atmosphere.

Data.—All available observations from Pyrton Hill, Ditcham Park, and Benson.

Height in kiloms.	Jan.-March.	April-June.	July-Sept.	Oct.-Dec.
0	-0·02	0·14	-0·02	0·33
1	0·54	0·28	0·31	0·56
2	0·82	0·49	0·56	0·76
3	0·79	0·79	0·72	0·77
4	0·86	0·89	0·75	0·83
5	0·85	0·89	0·81	0·87
6	0·84	0·92	0·83	0·85
7	0·87	0·87	0·87	0·85
8	0·91	0·81	0·87	0·86
9	0·81	0·45	0·88	0·78
10	0·35	0·20	0·43	0·29
11	-0·32	-0·12	-0·08	-0·24
12	-0·38	-0·24	-0·41	-0·34
13	-0·37	-0·01	-0·19	-0·50

These correlation coefficients, ranging as they do from 0·72 to 0·91 for the layers between 3*k* and 8*k*, present indisputably strong evidence of a very close relationship between pressure and temperature at the same level. Now it is easily proved that a correlation coefficient is always lowered in the numerical sense by errors of observation.† Hence a point of considerable importance arises with regard to the correlation coefficients of Table I. Granted that errors of observation exist in the observations from which the coefficients are calculated, what are the true values of these coefficients,

* "The Characteristics of the Free Atmosphere," W. H. Dines, F.R.S., 'Geophysical Memoirs,' No. 13, Meteorological Office, London, 1919.

† See pp. 34, 35, 'Computer's Handbook,' Section V, Sub-section 2, Meteorological Office, London, 1915.

the effects of errors of observation being eliminated? It is the aim of the present paper to answer this question from the data available for the purpose.

Correction of Coefficients of Correlation for Probable Errors of Observation.

There is first a piece of statistical theory to consider in its special application to our problem.

Suppose that we have a series of departures from a mean value. Let this series be $x_1, x_2, x_3, \dots, x_n$, the terms in the series being true values. Let the errors of observation be $a_1, a_2, a_3, \dots, a_n$, respectively. Then the observed values will be $x_1 + a_1, x_2 + a_2, x_3 + a_3, \dots, x_n + a_n$. The observed standard deviation will be σ_{x+a} where

$$\sigma_{x+a}^2 = \frac{\Sigma (x_1 + a_1)^2}{n} = \frac{\Sigma x_1^2}{n} + \frac{2\Sigma x_1 a_1}{n} + \frac{\Sigma a_1^2}{n} = \sigma_x^2 + \sigma_a^2,$$

since x and a are mutually independent.

Now let us suppose that we have a second series of departures from a mean value. Let this series be $y_1, y_2, y_3, \dots, y_n$. Let the errors of observation be $b_1, b_2, b_3, \dots, b_n$, respectively, so that the observed values are $y_1 + b_1, y_2 + b_2, y_3 + b_3, \dots, y_n + b_n$. We have as before $\sigma_{y+b}^2 = \sigma_y^2 + \sigma_b^2$ where σ_{y+b} is the observed standard deviation and σ_y the true standard deviation.

We shall now correlate the two series. The true correlation coefficient r_{xy} is given by $r_{xy} = \frac{\Sigma xy}{n\sigma_x\sigma_y}$.

The observed correlation coefficient

$$r_{x+a, y+b} = \frac{\Sigma (x+a)(y+b)}{n\sigma_{x+a}\sigma_{y+b}} = \frac{\Sigma xy}{n\sigma_{x+a}\sigma_{y+b}},$$

since x and b, y and a, a and b are mutually independent.

We have thus that

$$\frac{r_{xy}}{r_{x+a, y+b}} = \frac{\sigma_{x+a}}{\sigma_x} \cdot \frac{\sigma_y}{\sigma_{y+b}}.$$

But $\sigma_{x+a}^2 = \sigma_x^2 + \sigma_a^2$ and $\sigma_{y+b}^2 = \sigma_y^2 + \sigma_b^2$.

Hence we get

$$r_{xy}^2 = \frac{\sigma_x^2 + \sigma_a^2}{\sigma_x^2} \cdot \frac{\sigma_y^2 + \sigma_b^2}{\sigma_y^2} (r_{x+a, y+b})^2,$$

or

$$r_{xy}^2 = \left(1 + \frac{\sigma_a^2}{\sigma_x^2}\right) \left(1 + \frac{\sigma_b^2}{\sigma_y^2}\right) (r_{x+a, y+b})^2. \quad (1)$$

Thus, if we know the values of $\sigma_a/\sigma_x, \sigma_b/\sigma_y$ we can calculate the true correlation coefficient r_{xy} from the observed correlation coefficient $r_{x+a, y+b}$.

We shall now find values of $\sigma_a/\sigma_x, \sigma_b/\sigma_y$ for temperature and pressure observations in the free atmosphere. Suppose that we have a series of

temperature observations at a certain level. Let the true values of these temperature readings be $X_1, X_2, X_3, \dots, X_n$. Let the errors of observation be $a_1, a_2, a_3, \dots, a_n$ so that the observed readings are $X_1 + a_1, X_2 + a_2, X_3 + a_3, \dots, X_n + a_n$. Now, let us put a restriction on the errors of observation of our temperature readings in this way, let the maximum possible error be k times the true reading, *i.e.*, $a_1 \nless kX_1, a_2 \nless kX_2$, and so on. Suppose that the greatest term in the X series is X_g . Then the errors of observation will have a range from $-kX_g$ to kX_g , the mean error being zero since positive and negative errors are equally likely. Thus the range of errors of observation is $2kX_g$. But if σ_a be the standard deviation in our " a " series this range is approximately $6\sigma_a$, since errors of observation follow the normal law and $m \pm 3\sigma$ practically covers the whole in a normal distribution, m being the mean and σ the standard deviation. We have then

$$6\sigma_a = 2kX_g \quad \text{or} \quad 3\sigma_a = kX_g.$$

Now our X series is a series of temperature readings which are likely to be distributed according to the normal law. If we write $\bar{x}$ for the mean of this X series, a close approximation to the value of X_g would be given by $X_g = \bar{x} + 3\sigma_x$. With this value of X_g we get:—

$$3\sigma_a = k(\bar{x} + 3\sigma_x) \quad \text{or} \quad \frac{\sigma_a}{\sigma_x} = \frac{k}{3} \left(\frac{\bar{x}}{\sigma_x} + 3 \right). \quad (2)$$

Now suppose that we have a series of pressure readings taken at the same levels as our temperature readings. Let our pressure series be $Y_1, Y_2, Y_3, \dots, Y_n$, Y_1 being taken at the same time as X_1, Y_2 as X_2 , and so on. Let the errors of observation in our Y series be $b_1, b_2, b_3, \dots, b_n$, respectively. Let us assume that $b_1 \nless lY_1, b_2 \nless lY_2$, etc. We shall then have

$$\frac{\sigma_b}{\sigma_y} = \frac{l}{3} \left(\frac{\bar{y}}{\sigma_y} + 3 \right). \quad (3)$$

Then, if we know the values of $\bar{x}/\sigma_x$ and $\bar{y}/\sigma_y$, equation (2) will give us the value of σ_a/σ_x in terms of k , and equation (3) will give us the value of σ_b/σ_y in terms of l . We should then be able to substitute these values of $\sigma_a/\sigma_x, \sigma_b/\sigma_y$ in equation (1), and thus obtain the value of the true correlation coefficient r_{xy} , between pressure and temperature at the same level, in terms of k and l and the observed correlation coefficient $r_{x+a, y+b}$.

Estimation of the Probable Errors of Measurement of Temperature and Pressure in the Upper Air.

From Dines' figures,* average values of $\bar{x}/\sigma_x$ (temperature) and $\bar{y}/\sigma_y$ (pressure) for the year are as given in Table II.

* See pp. 11, 12, 'Quart. Jour. Roy. Met. Soc.,' vol. 40, No. 169, January, 1914.

Table II.—Average Values of $\bar{a}/\sigma_x$ (temperature) and $\bar{b}/\sigma_y$ (pressure) for Winter (Nov.–April), 36 observations, and Summer (May–Oct.), 50 observations.

Height in kilom.	$\bar{x}/\sigma_x$		$\bar{y}/\sigma_y$		σ_a/σ_x from equation (2)		σ_b/σ_y from equation (3).	
	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.
2	47.0	44.5	59.4	69.4	16.74	15.84	20.81	24.11
4	39.5	44.3	45.9	51.7	14.24	15.84	16.31	18.21
6	37.4	42.7	38.9	38.6	13.54	15.24	14.01	13.91
8	42.4	41.2	32.7	36.8	15.14	14.74	11.91	18.31
10	48.7	34.8	30.0	31.4	17.24	12.64	11.01	11.51

A curious result may be noticed in Table II. If k and l were constant, the values of σ_a/σ_x (temperature) in summer, and σ_b/σ_y (pressure) in winter and summer would decrease with increasing height. The values of σ_a/σ_x in winter, however, would decrease from 2 to 6 kilom., and then increase from 6 to 10 kilom.

According to W. H. Dines,* there is good reason to suppose that the probable error of a recorded temperature in the upper air does not exceed 1°C . Now, as we have already stated, $m \pm 3\sigma$ practically covers the range of observations in a normal distribution, m being the mean and σ the standard deviation. Since $\sigma = \frac{2}{3}e$ approximately, where e is the probable error, we can write this range as $m \pm 9e/2$. Putting $e = 1^\circ\text{C}$, we get 4.5°C . for our maximum error expressed as excess over mean. On a true mean temperature of 265°A ., this gives us a value of $k = 4.5/265 = 0.017$, or approximately 0.02. Let us assume, then, 0.02 as a value of k , and, as seems reasonable enough, let us assume the same value for l . Putting $k = l = 0.02$ in Table II, and substituting the values obtained for σ_a/σ_x and σ_b/σ_y in equation (1), we get the equations of Table III.

The equations of Table III can be applied directly to the correlation coefficients of Table I. The winter equations can be used for the trimesters January–March, October–December, and the summer equations for the trimesters April–June, July–September, without appreciable error. Calculated in this way, the true correlation coefficients between temperature and pressure at the same level are as given in Table IV.

Table IV presents some very striking features. The highest corrected coefficients are for the trimester April–June at heights of 4 and 6 kilom. These coefficients are 0.997 and 0.994 respectively. If the assumptions we have made can be justified, then we have every reason to assert that the

* See p. 30, 'Computer's Handbook,' Section II, Meteorological Office, London, 1917.

Table III.—Values of True Correlation Coefficients, r_{xy} , in terms of observed correlation coefficients, $r_{x+a, y+b}$, for maximum possible errors of observation in both temperature and pressure readings of 2 per cent. of true readings.

Height in kilom.	Winter.	Summer.
2	$r_{xy} = 1 \cdot 14 r_{x+a, y+b}$	$r_{xy} = 1 \cdot 16 r_{x+a, y+b}$
4	$= 1 \cdot 09$ "	$= 1 \cdot 12$ "
6	$= 1 \cdot 07$ "	$= 1 \cdot 08$ "
8	$= 1 \cdot 07$ "	$= 1 \cdot 08$ "
10	$= 1 \cdot 08$ "	$= 1 \cdot 06$ "

Table IV.—True Correlation Coefficients between temperature and pressure at the same level, calculated from the observed correlation coefficients of Table I, on the assumption that both temperature and pressure readings are subject to maximum possible errors of 2 per cent. of true values.

Height in kilom.	2.	4.	6.	8.	10.
January–March	0·935	0·937	0·899	0·974	0·378
April–June	0·568	0·997	0·994	0·875	0·212
July–September	0·650	0·840	0·905	0·940	0·466
October–December	0·866	0·905	0·910	0·921	0·313

relation of change of temperature to change of pressure at the same level is practically that of direct proportionality during the trimester April–June at heights 4 to 6 kiloms. The same assertion may also be made for the trimester January–March for height 8 kilom., the corrected coefficient in this case being 0·974. Table IV can be summarised in the statement that, throughout the year, from 4 to 8 kilom. the relationship between change of temperature and change of pressure at the same level is an exceedingly close one, being sometimes, but not always that of direct proportionality.

Further Inquiry into the Magnitude of the Probable Error.

The results of Table IV are sufficiently encouraging to warrant our proceeding to obtain more definite information as to the possible values of errors of observation of pressure and temperature readings in the upper air. This we shall do in the next part of the paper.

Neglecting the variation of gravity with height, and the effect of humidity on the density of the air, the pressure-temperature-height equation may be written

$$h = \frac{T_m}{0\cdot014837} \log \frac{P_0}{P_1}, \quad (4)$$

where P_0 is the pressure at the surface,

P_1 is the pressure at height h metres,

and T_m is the harmonic mean temperature of the air column from the surface to height h metres.

Suppose that T_m is found from n temperature readings taken at equal intervals of height, and that the true values of these n readings are $T_1, T_2, T_3, \dots, T_n$. Let these true readings be subject to errors of observation, each error of observation being within k times the true reading. Then if T_m' were the maximum possible observed value of T_m we should have

$$\begin{aligned} \frac{n}{T_m'} &= \frac{1}{T_1 + kT_1} + \frac{1}{T_2 + kT_2} + \dots + \frac{1}{T_n + kT_n} \\ &= \frac{1}{1+k} \left[\frac{1}{T_1} + \frac{1}{T_2} + \dots + \frac{1}{T_n} \right] = \frac{1}{1+k} \cdot \frac{n}{T_m}. \end{aligned}$$

Hence

$$T_m' = (1+k)T_m.$$

Then, if there were no errors of observation in the pressures P_0 and P_1 , we should get the maximum possible observed height h' , where

$$h' = \frac{(1+k)T_m}{0.014837} \log \frac{P_0}{P_1} = (1+k)h \dots \text{from (4).}$$

In the same way we should get the minimum possible observed height h'' where

$$h'' = (1-k)h.$$

Thus, if there were no errors of observation in pressure, and the errors of observation in temperature were not greater than k times the true reading in each case, we have a possible range $\pm kh$ for errors in height where h is the true height.

Let us now assume a possible error of observation in pressure of l times the true value in each case. Then the maximum value of $\log P_0/P_1$, P_0 and P_1 being true values, would be $\log P_0(1+l)/P_1(1-l)$, and the minimum value $\log P_0(1-l)/P_1(1+l)$. Supposing there to be no error in temperature, h''' , the maximum value of the observed height, would be given by

$$\begin{aligned} h''' &= \frac{T_m}{0.014837} \log \frac{P_0(1+l)}{P_1(1-l)} \\ &= \frac{T_m}{0.014837} \left[\log \frac{P_0}{P_1} + \log \frac{1+l}{1-l} \right] = h + \frac{T_m}{0.014837} \log \frac{1+l}{1-l}. \end{aligned}$$

In the same way h'''' the minimum value of the observed height would be given by

$$h'''' = h + \frac{T_m}{0.014837} \log \frac{1-l}{1+l}.$$

If, now, we have errors of observation in temperature up to k times the true values, and at the same time errors of observation in pressure up to l times the true values, h_1 , the maximum value of the observed height would be given by

$$\begin{aligned} h_1 &= \frac{(1+k) T_m}{0.014837} \log \frac{P_0(1+l)}{P_1(1-l)} = \frac{(1+k) T_m}{0.014837} \left[\log \frac{P_0}{P_1} + \log \frac{1+l}{1-l} \right] \\ &= (1+k) \left[h + \frac{T_m}{0.014837} \log \frac{1+l}{1-l} \right]. \end{aligned}$$

The minimum value of the observed height would be given by

$$h_2 = \frac{(1-k) T_m}{0.014837} \log \frac{P_0(1-l)}{P_1(1+l)} = (1-k) \left[h + \frac{T_m}{0.014837} \log \frac{1-l}{1+l} \right],$$

h being the true height in each case.

The range over which the observed height could vary would be given by

$$\begin{aligned} h_1 - h_2 &= (1+k) \left[h + \frac{T_m}{0.014837} \log \frac{1+l}{1-l} \right] - (1-k) \left[h + \frac{T_m}{0.014837} \log \frac{1-l}{1+l} \right] \\ &= 2kh + \frac{T_m}{0.014837} [(1+k) \log(1+l) - (1+k) \log(1-l) \\ &\quad + (1-k) \log(1+l) - (1-k) \log(1-l)] \\ &= 2kh + \frac{T_m}{0.014837} [2 \log(1+l) - 2 \log(1-l)] \\ &= 2kh + \frac{2T_m}{0.014837} \log \frac{1+l}{1-l}. \end{aligned} \tag{5}$$

Prof. W. R. Blair* has given the results of a series of registering balloon ascents made in America, in which the balloons were followed by two theodolites and the heights calculated by triangulation, as well as from the temperature-pressure records of the instruments. Since the base-line used was 5088 metres (over 3 miles), the heights found by triangulation must be fairly accurate, and we can reasonably take them to be true values. In Table V are given those of Prof. Blair's results of which direct use is made in this paper.

* "Free Air Data by Means of Sounding Balloons," 'Monthly Weather Rev.,' vol. 44, p. 247, Washington (1916).

Table V.

Professor Blair's observations.			Assumptions made in this paper.	
Height from temperature-pressure record.	Heights from triangulation.		True height.	Range over which observed height can vary when calculated from temperature-pressure-height equation.
	Lowest.	Highest.		
Metres.	Metres.	Metres.	Metres.	Metres.
3000	2900	3250	3000	350
6000	5830	6530	6000	700
9000	8870	9460	9000	590

If, then, we put $h_1 - h_2 = 350$, and $k = 3000$ in equation (5), and assume a harmonic mean temperature of 275° A. for the air column 0–3000 metres, we get

$$350 = 2 \times 3000k + \frac{2 \times 275}{0.014837} \log \frac{1+l}{1-l}.$$

It is convenient to reduce this equation to the form

$$\log \frac{1+l}{1-l} = 0.009442 - 0.16186k. \quad (6)$$

Since l is positive $\log 1+l/(1-l)$ is positive and therefore we must have

$$0.16186k < 0.009442 \quad \text{i.e., } k < 0.058.$$

Also, since k is positive, the maximum value of $\log 1+l/(1-l)$ is 0.009442, i.e., the maximum value of $1+l/1-l$ is 1.022. This gives a maximum value of $l = 0.0109$. If we put $k = 0.01$ in equation (6), we get $l = 0.009$, $k = 0.02$ gives us $l = 0.007$, $k = 0.03$ gives us $l = 0.005$, for $k = 0.04$ we have $l = 0.003$, and for $k = 0.05$ we get the value $l = 0.0015$.

When $h = 6000$ metres, we have $h_1 - h_2 = 700$ metres. Hence, from equation (5), assuming a harmonic mean temperature of 265° A. for the air column 0–6000 metres, we get

$$700 = 2 \times 6000k + \frac{2 \times 265}{0.014837} \log \frac{1+l}{1-l}.$$

This equation reduces to

$$\log \frac{1+l}{1-l} = 0.0196 - 0.3360k. \quad (7)$$

Reasoning, as before, we get a maximum value for k , 0.058, and for l , 0.022. Other values of k and l from equation (7) are $k = 0.01$, $l = 0.018$; $k = 0.02$, $l = 0.015$; $k = 0.03$, $l = 0.012$; $k = 0.04$, $l = 0.007$; $k = 0.05$, $l = 0.003$.

At 9000 metres, we have from equation (5)

$$590 = 2 \times 9000k + \frac{2 \times 255}{0.014837} \log \frac{1+l}{1-l}$$

assuming a harmonic mean temperature of 225° A. for the air column 0 to 9000 metres.

This equation reduces to

$$\log \frac{1+l}{1-l} = 0.1485 - 0.5238k. \quad (8)$$

From this equation, the maximum value of k is 0.028, and the maximum value of l , 0.017. Other values are $k = 0.01$, $l = 0.011$; $k = 0.02$, $l = 0.005$.

It will be convenient to tabulate the corresponding values of k and l . This is done in Table VI.

Table VI.—Possible Values of k and l . If T and P be *true* readings of temperature and pressure at the same level, kT and lP are the maximum possible errors of observation in T and P respectively.

3000 metres (14 ascents).		6000 metres (9 ascents).		9000 metres (4? ascents).	
k .	l .	k .	l .	k .	l .
0.00	0.011	0.00	0.022	0.00	0.017
0.01	0.009	0.01	0.018	0.01	0.011
0.02	0.007	0.02	0.015	0.02	0.005
0.03	0.005	0.03	0.012	0.028	0.00
0.04	0.0034	0.04	0.007		
0.05	0.0015	0.05	0.003		
0.058	0.00	0.058	0.00		

From the numerical values given in Table VI, we can assume certain possible values of k and l for the layer of the atmosphere from 3 to 9 kilom. We shall not lay much stress on the values given for height 9000 metres, since the number of observations for that height is small. If $k = 0$, a reasonably possible value of l is 0.02. Assuming $k = 0$ and $l = 0.02$, from Table II and equation (1) we get the results given in Table VII.

Table VII.— $k = 0$, $l = 0.02$, *i.e.*, no errors in temperature readings, maximum possible error in pressure readings 2 per cent. of true values.

Height in kilom.	Values of α where $r_{xy} = \alpha r_{x+a, y+b}$, see equation (1).	
	Winter.	Summer.
2	1.08	1.11
4	1.05	1.06
6	1.04	1.04
8	1.03	1.03
10	1.02	1.03

In calculating the results set out in Table VII, we assumed that there were no errors of observation in temperature readings. Let us now assume that there are no errors of observation in pressure readings, *i.e.*, let us assume $l = 0.00$. From Table VI we get a value of $k = 0.05$, corresponding to $l = 0.00$. Putting $k = 0.05$, $l = 0.00$, from Table II and equation (1) we get the results given in Table VIII.

Table VIII.— $k = 0.05$, $l = 0.00$, *i.e.*, maximum possible error in temperature readings 5 per cent. of true values, no errors in pressure readings.

Height in kilom.	Values of α where $r_{xy} = \alpha r_{x+a, y+b}$, see equation (1).	
	Winter.	Summer.
2	1.30	1.28
4	1.23	1.28
6	1.21	1.26
8	1.25	1.24
10	1.32	1.18

It is instructive to compare Tables VII and VIII, and to see from such a comparison that there is a distinct possibility of errors of observation in temperature having a much more marked effect than errors of observation in pressure in increasing the observed correlation coefficients of Table I.

The numerical quantity which we have called α is defined by the relationship $r_{xy} = \alpha r_{x+a, y+b}$, r_{xy} being the true correlation coefficient between temperature and pressure at the same level when errors of observation in both elements have been eliminated, and $r_{x+a, y+b}$ being the observed correlation coefficient. All the values of α which have been calculated in connection with the work of this paper are given in Table IX.

Reference to Table IV shows us the true correlation coefficients between temperature and pressure at the same level, obtained by using the values of α corresponding to $k = l = 0.02$. It is clear that, to get higher values of the true correlation coefficients than those of Table IV, we must use higher values of α than those corresponding to $k = l = 0.02$. Such higher values of α , on the whole, are found in Table IX, corresponding to (i) $k = 0.03$, $l = 0.00$; (ii) $k = 0.03$, $l = 0.01$; (iii) $k = 0.04$, $l = 0.00$; (iv) $k = 0.05$, $l = 0.00$.

Since it is hardly likely that pressure readings will be subject to no error whatever, we can neglect (i), (iii) and (iv) in which $l = 0.00$. The remaining case, (ii) $k = 0.03$, $l = 0.01$, gives us a maximum possible error

Table IX.—Values of α , where $r_{xy} = \alpha'x + \alpha_y y + b$ for possible values of k and l , as shown in Table VI.

k .	l .	2 kilom.		4 kilom.		6 kilom.		8 kilom.		10 kilom.	
		Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.	Winter.	Summer.
0.00	0.01	1.02	1.03	1.01	1.02	1.01	1.01	1.01	1.01	1.01	1.01
0.00	0.02	1.08	1.11	1.05	1.06	1.04	1.04	1.03	1.03	1.02	1.02
0.01	0.01	1.04	1.04	1.02	1.03	1.02	1.02	1.02	1.02	1.02	1.02
0.01	0.02	1.10	1.12	1.06	1.08	1.05	1.05	1.04	1.05	1.04	1.03
0.02	0.01	1.08	1.08	1.05	1.07	1.05	1.05	1.05	1.05	1.06	1.04
0.02	0.02	1.14	1.16	1.09	1.12	1.07	1.08	1.07	1.08	1.08	1.06
0.03	0.00	1.12	1.11	1.09	1.11	1.08	1.10	1.10	1.09	1.12	1.07
0.03	0.01	1.14	1.14	1.10	1.13	1.09	1.10	1.10	1.10	1.13	1.08
0.04	0.00	1.12	1.18	1.15	1.18	1.14	1.14	1.17	1.16	1.21	1.12
0.05	0.00	1.30	1.28	1.23	1.28	1.21	1.21	1.26	1.24	1.32	1.18

of observation in a temperature reading of 3 per cent. of the true value and a maximum possible error of observation in a pressure reading of 1 per cent. of the true value. With ordinary temperatures and pressures in the upper air this would mean admitting a maximum possible error in temperature of about $8\frac{1}{2}^{\circ}$ C., and a maximum possible error in pressure of 8 mb. We must emphasise the fact that these are maximum possible errors which would seldom occur. The corresponding probable errors would be just under 2° C. and 2 mb. If Prof. Blair's observations are correct, and our calculations based on those observations are correct, such errors are certainly possible.

The Corrected Values of the Coefficients.

Assuming, then, that we can have $k = 0.03$, $l = 0.01$, we obtain certain possible values of α from Table IX. These values of α are given for 2, 4, 6, 8, 10 kilom. By interpolation, we can get values of α for 3, 5, 7, 9 kilom. Applying these values of α to the correlation coefficients of Table I, we get the true correlation coefficients of Table X.

Table X.—True Correlation Coefficients between Pressure and Temperature at the same level, assuming a maximum possible error in temperature readings of 3 per cent., and in pressure readings of 1 per cent. of the true value.

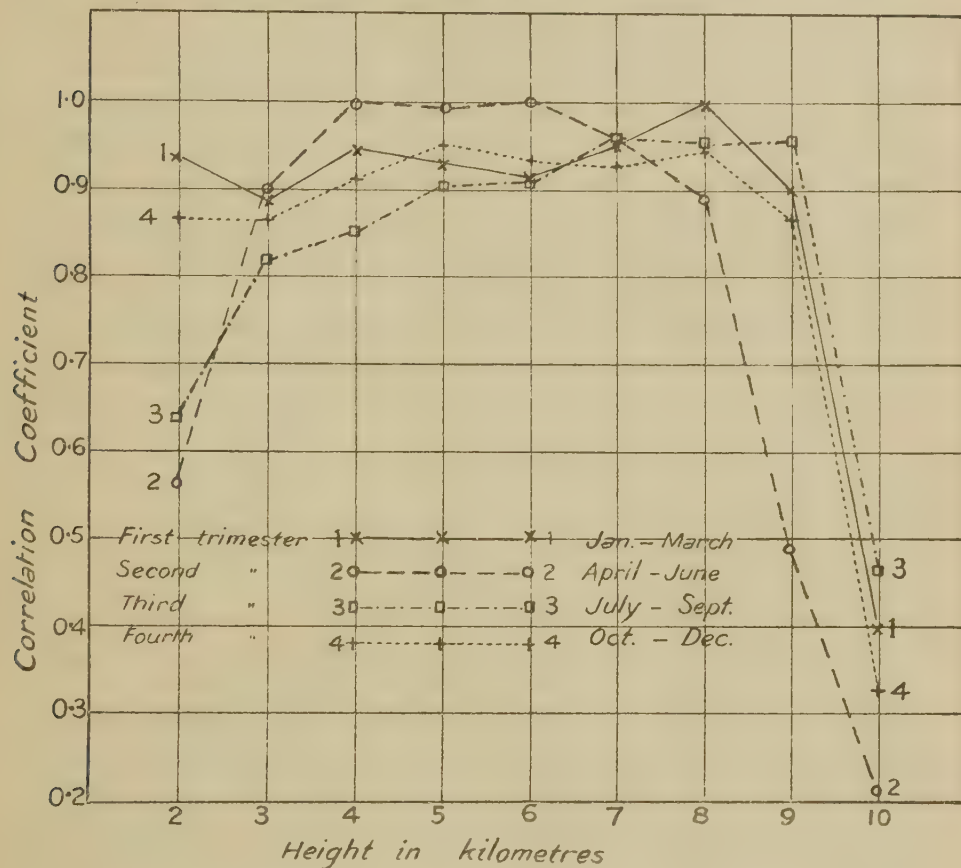
Height in kilom.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Jan.—March	0.935	0.885	0.946	0.931	0.916	0.953	1.000	0.903	0.400
April—June	0.559	0.900	1.000	0.992	1.000	0.957	0.891	0.491	0.216
July—Sept.	0.638	0.817	0.848	0.903	0.913	0.957	0.957	0.959	0.464
Oct.—Dec.	0.866	0.862	0.913	0.953	0.935	0.931	0.986	0.870	0.328

If the assumptions and calculations of this paper are correct (and there appears to be no reason to doubt them), we have obtained some striking results in Table X. Three of the coefficients in that Table are actually unity. Even if we cannot conclude that the relationship between pressure and temperature at the same level is *always* that of direct proportionality, we have proved that it is so at 4 and 6 kilom. for the first three months of the year, and at 8 kilom. for the second three months.

The correlation coefficients of Table X are shown graphically in the accompanying figure.

The present paper had its origin in a suggestion made to me by Sir Napier Shaw, F.R.S. I am glad to have this opportunity of expressing my thanks

to Sir Napier for his original suggestion, and also for subsequent suggestions, which led to the calculation of the correlation coefficients of Tables IV



and X. I cannot do better than conclude the paper by quoting the following remarks made by Sir Napier when the paper was submitted to him:—

“The least that can be said about the extraordinary results of Table X is that the relation of change of temperature to change of pressure has been proved to be that of direct proportionality at 4 kilom. and 6 kilom. in the second trimester and at 8 kilom. in the first trimester, while from 3 to 8 kilom. during the whole year the departure from proportionality is never more than 20 per cent.

“It would, therefore, be very profitable to consider what it is that in certain trimesters spoils the relation which is obviously operative in others. We know, for example, that there is a seasonal variation of pressure and temperature at all levels, so that there must be presumably a seasonal change

in the constant of the regression-equation within a trimester which will affect the coefficients. We know also that at the surface there are specimens of air at the same pressure with very different temperatures; and if these specimens passed to the pressure of the assigned levels by change of pressure alone, the same pressures would have different temperatures at those levels. Hence in random sampling one might get temperature changes without pressure changes, and *vice versâ*. Also the water-content of the atmosphere has a great influence upon the temperature change due to pressure change. Further, Dines has indicated that if at any level isobars are also isotherms, there is no change of wind with height. This is sometimes true for a considerable range of height, sometimes not. Why?

The present paper is an invitation to somebody to take the next step in explaining the departures from these laws of the upper atmosphere.

On the Absorption and Scattering of Light.

By SIR ARTHUR SCHUSTER, F.R.S.

(Received October 28, 1920.)

When a beam of light passes through a material medium it suffers gradual extinction, mainly through molecular scattering, but partly also through conversion into heat. The two processes should be clearly distinguished, as there is some danger of confusing the issue if the term "absorption" is applied to what is a mere diversion of the light energy from its original direction.

It is easy enough to form an idea of the mechanism involved in scattering, but the process of absorption is more difficult to represent analytically. In order to obtain a clearer view of its fundamental features, I propose to discuss the transmission of light through a medium the molecules of which have only one free period of vibration.

We may base the discussion on the differential equation defining the position of an oscillator

$$\ddot{z} + 2kz + n^2z = F \cos \omega t. \quad (1)$$

Its well-known solution is

$$z = \frac{F \sin \epsilon}{2k\omega} \cos(\omega t - \epsilon) + Ce^{-kt} \sin \sqrt{(n^2 - k^2)}(t - t_1), \quad (2)$$

where

$$\tan \epsilon = 2\omega k / (n^2 - \omega^2).$$

For subsequent use we may express the first term in a more convenient form. Writing $R = F \cos \omega t$, put :

$$z = AR - B\omega^{-1} \frac{dR}{dt},$$

where $A = \sin \epsilon \cos \epsilon / 2\omega k$; $B = \sin^2 \epsilon / 2\omega k$; (3)

from which we find

$$A^2 + B^2 = \sin^2 \epsilon / 4\omega^2 k^2 = B / 2\omega k. \quad (4)$$

If in (1) $F = 0$, we obtain what is called the free vibration, and its mathematical expression suggests that the frictional term has lengthened the period in the ratio of $n/\sqrt{(n^2 - k^2)}$. I desire, in the first place, to challenge this interpretation. It has a substantial meaning when we can follow with our eyes the movement of a material body such as that of a damped galvanometer needle, but in the case of a luminous disturbance the only means at our disposal to determine its periods is to analyse the light by spectroscopic methods, and the first and obvious conclusion to be drawn is that the factor e^{-kt} destroys the homogeneity of the light. In the language of the spectroscopist, the light is no longer concentrated into a line, but drawn out into a band. The band, no doubt, is narrow when k is small compared with ω , and the original statement might still be justified if $(2\pi)^{-1}\sqrt{(n^2 - k^2)}$ were the frequency for which the intensity is a maximum. But, as will be shown, this is not true. In the problem here considered, the maximum of the intensity, on the contrary, takes place at a frequency $n/2\pi$, and is therefore the same as if there were no frictional term.

I return to equations (1) and (2), in order to bring them into closer connection with the actual problem to be treated. We never deal with a perfectly homogeneous source of light, and the right-hand side should therefore not be confined to a single value of ω . In the important case of white light, we substitute in (1) $\int_0^\infty E \cos \omega(t - \theta) d\omega$ for $F \cos \omega t$, with the proviso that θ will depend on ω in a perfectly irregular manner. The value of E also fluctuates, but its average value in the neighbourhood of a particular value of ω will be determined by the distribution of intensities along the spectrum of the incident light. We may provisionally treat it as constant, because in problems of light the value of k is very small, so that the oscillations are only appreciable in the immediate neighbourhood of $n - \omega = 0$. The distribution of intensities in the rest of the spectrum does not matter.

During their motion the particles are subject to the influence of other molecules, which may act through impacts and therefore be discontinuous.

We must therefore add to the second term of (2) a number of similar expression, and the completed equation now becomes

$$z = \int_0^\infty E d\omega [(n^2 - \omega^2)^2 + 4\omega^2 k^2]^{-\frac{1}{2}} \cos(\omega t - \epsilon) + \sum C_s e^{-k(t-t_s)} \sin m(t-t_s), \quad (5)$$

where m^2 stands for $n^2 - k^2$, and the summation includes all values of t_s at which the velocity becomes discontinuous, owing to molecular encounters. Each term comes into effect at time $t = t_s$, when it contributes an initial velocity $C_s m$. The phase ϵ is not the same as in (2), but depends on θ .

My proposition now is that all the terms of (5) are spectroscopically identical. They represent disturbances which, when analysed by a prism or grating, can differ only by a constant multiplier, the relative values of the intensities along the spectrum being the same. To those familiar with the view, first suggested by Gouy and the late Lord Rayleigh, that white light may be represented as consisting of a series of discontinuous and irregularly distributed impulses, and that, when the intensities within unit range of frequency are constant along the spectrum, these impulses are of infinitely short duration, the proposition which I have stated will be self-evident. There can be no distinction between the effect of the impulses due to light and those that have their origin in molecular encounters. Any discrimination between forced and free vibrations when white light is the source of energy ceases to have a meaning.

The spectroscopical identity of the different terms of (5) is of some importance in illustrating the proportionality of radiation and absorption in enclosures of uniform temperature. The extinction of the transmitted beam depends entirely on the first term, radiation to some extent on the others; they must therefore all show the same distribution of intensities for different frequencies if the proportionality is to hold.

Those to whom the above reasoning is not convincing, must take the longer path of applying Fourier's integrals:—

Let z be a function having zero value up to time, and then to continue as $Ce^{-kt} \sin mt$, so that $v = mC$ is the initial velocity. By Fourier's theorem,

$$\pi z = C \int_0^\infty d\omega \int_0^\infty e^{-k\lambda} \sin m\lambda \cos \omega(\lambda - t) d\lambda. \quad (6)$$

$$\text{Let } A' = \int_0^\infty d\lambda (\sin m\lambda \cos \omega\lambda) e^{-k\lambda}; \quad B' = \int_0^\infty d\lambda (\sin m\lambda \sin \omega\lambda) e^{-k\lambda}$$

$$\text{and put } P = [(m + \omega)^2 + k^2]^{-1}; \quad Q = [(m - \omega)^2 + k^2]^{-1};$$

from which it follows that

$$P + Q = 2(n^2 + \omega^2)PQ; \quad Q - P = 4m\omega PQ$$

and

$$(PQ)^{-1} = (n^2 - \omega^2)^2 + 4k^2\omega^2.$$

By integration we find

$$2A' = m(P+Q) + \omega(P-Q); \quad 2B' = k(Q-P),$$

$$\therefore \quad A' = m(n^2 - \omega^2)PQ; \quad B' = 2mk\omega PQ.$$

Equation (6) then becomes

$$\pi z = C \int_0^\infty d\omega (A' \cos \omega t + B' \sin \omega t) = v \int_0^\infty d\omega S \cos(\omega t - \alpha)$$

where

$$S = [(n^2 - \omega^2)^2 + 4k^2\omega^2]^{-\frac{1}{2}}.$$

This proves the proposition, for it shows that, for all positive values of t ,

$$Ce^{-kt} \sin mt = \pi^{-1} v \int_0^\infty d\omega [(n^2 - \omega^2)^2 + 4\omega^2 k^2]^{-\frac{1}{2}} \cos(\omega t - \epsilon),$$

where $\tan \epsilon = 2k\omega/(n^2 - \omega^2)$. For negative values of t , the right-hand side is zero. By a proper adjustment of the origin of time and of the constants, the integral can therefore be made to represent any term which appears in the summation on the right-hand side of (5).

If ϵ be a variable depending on ω , the motion ceases to be discontinuous, and may be made to represent an endless series of waves, such as constitutes white light, but this does not affect the distribution of energy among its constituents. Confining ourselves to the first term of (5), we obtain by differentiation

$$\frac{dz}{dt} = - \int_0^\infty E\omega d\omega [(n^2 - \omega^2)^2 + 4\omega^2 k^2]^{-\frac{1}{2}} \sin(\omega t - \epsilon),$$

the intensities to be assigned to a range of frequency, $d\omega$, are, by a theorem of the late Lord Rayleigh,* proportional to

$$E^2\omega^2 [(n^2 - \omega^2)^2 + 4\omega^2 k^2]^{-1} d\omega.$$

It is easily seen that the maximum takes place when $n = \omega$, and this applies to the oscillation defined by the second term of (2).

The investigation has been given in a form which applies equally to the electromagnetic theory in which equation (1) is only approximately correct. According to Planck and Abraham, in the absence of outer forces, we must replace (1) by:

$$\frac{d^2 z}{dt^2} - 2\sigma \frac{d^3 z}{dt^3} + n^2 z = 0.$$

Assuming a solution of the form e^{pt} , where p is complex, the condition to be satisfied is

$$p^2 + 2\sigma p^3 + n^2 = 0.$$

The constant σ , as will appear, is very small, and neglecting, therefore, the

* 'Scientific Papers,' vol. 3, p. 268.

middle term, we obtain, as a first approximation, $p = \pm in$. Substituting, therefore, $-n^2$ for p^2 in the middle term, we find, as a second approximation,

$$p^2 + 2\sigma n^2 p + n^2 = 0,$$

which gives, writing $\sigma n^2 = k$, as a second approximation,

$$p = -k \pm i\sqrt{(n^2 - k^2)},$$

and hence

$$z = e^{-kt} \cos [\sqrt{(n^2 - k^2)}(t - \alpha)].$$

The previous equations may therefore be applied with the proviso that k is now proportional to the square of the frequency.

A few words should be said on the numerical value of k . For a simple oscillator carrying an electric charge, the total energy radiated into space is known. If U be the energy of the oscillator, it is found that $U^{-1}dU/dt = 2c^2\omega^2/3\rho c$, where ρ is the mass of the electron and c the velocity of light. The diminution of energy being proportional to e^{-2kt} , the value of k is given by $c^2\omega^2/3\rho c$. Hence k/ω in terms of the wave-length is $2\pi c^2/3\rho\lambda$. Substituting 2.3×10^{-13} for c^2/ρ , we find for k/ω the value $5 \times 10^{-13}/\lambda$. For blue light, this is of the order 10^{-8} . For the constant σ , which occurs in the electromagnetic theory, we have $k = \sigma\omega^2$, which gives $\sigma = 2.5 \times 10^{-23}$. The small value of k enables us to conclude that it can only affect our calculations in the region in which n is so nearly equal to ω that our spectroscopic appliances cannot distinguish between them. In explaining the so-called anomalous dispersion, k can be left out of account altogether.

As regards the rate of propagation of waves through such a medium as we are considering, it is important to notice that while the terms of equation (3) are spectroscopically identical there is this important difference: the phases of the terms under the summation are independent of the incident light, but those which are under the integral sign are determined by it. Each light impulse produces a molecular oscillation which is definitely related to it, and combines with it in forming the wave-front. This accounts for the retardation which determines the refractive index.

In order to show more clearly the effect of scattering on wave-propagation, we must return to the consideration of the analytical expression for the forced vibration due to homogeneous light. The differential equation for the electric vector (R), transmitted through a non-conducting medium, containing N oscillators is

$$K \frac{d^2 R}{dt^2} + 4\pi N e \frac{d^2 \zeta}{dt^2} = \frac{d^2 R}{dx^2}.$$

If the changes of the optical properties of a medium be entirely due to the

oscillators, the wave must be propagated as in vacuo if $N = 0$. Hence we may write c^{-2} for k .

Assuming the disturbance to be simply periodic, the displacement has two components, one in phase with R and the other in phase with dR/dt , and we may therefore write

$$4\pi\zeta = AR - B\omega^{-1} \frac{dR}{dt}.$$

If λ be the wave-length, a solution of the form

$$R = R_0 e^{-2\pi\kappa x/\lambda} \cos \{2\pi\mu(x - c_1 t)/\lambda\} \quad (7)$$

leads to the conditions

$$\left. \begin{aligned} \mu^2 - \kappa^2 - 1 &= N A e c^2 \\ 2\mu\kappa &= N B e c^2 \end{aligned} \right\}. \quad (8)$$

We may draw from these equations the important conclusion that if κ^2 be negligible the refractive index depends entirely on the component of ζ , which is in phase with R , and that the coefficient of extinction depends mainly on the component at right angles to R . The values of A and B may be written down from (3), remembering that $4\pi\zeta$ now replaces z , and that the factor e/ρ should be applied on the right-hand side of (1) if the equation is to represent correctly the motion of an electron having mass ρ . Hence (4) becomes:

$$k\omega\rho(A^2 + B^2) = 2\pi e B. \quad (9)$$

The three equations (8) and (9) allow us to eliminate A and B . The exponential factor in (7) shows that unless the body absorbs an appreciable portion of the light when the thickness is a fraction of a millimetre, the value of κ is small. Neglecting, therefore, in the first instance κ^2 , the first equation gives

$$(\mu^2 - 1)^2 = N^2 (A^2 + B^2) e^2 c^4, \quad (10)$$

while the second equation combined with (9) gives

$$2\mu\kappa = (2\pi)^{-1} N (A^2 + B^2) k\omega\rho c^2. \quad (11)$$

Hence

$$(\mu^2 - 1)^2 = 4\pi\mu\kappa e^2 c^2 N / k\omega\rho. \quad (12)$$

The value of k is determined by the radiation of an electric oscillator. It has already been referred to as equal to $e^2\omega^2/3\rho c_1$, where c_1 is equal to the velocity of light in the medium. Remembering that c/c_1 is equal to μ equation (10) can be brought into the form

$$4\pi\kappa\lambda^{-1} = \frac{(\mu^2 - 1)^2 \omega^4}{6\pi N e^4}. \quad (13)$$

The left-hand side represents the coefficient of extinction of the intensity of light, and if on the right-hand side ωc^{-1} be expressed in terms of the wave-length, the equation is identical with Lord Rayleigh's, provided that

$\mu-1$ is small, so that $\mu^2-1 = 2(\mu-1)$ with a sufficient degree of accuracy. If higher powers of κ are to be taken into account $(\mu^2 + \kappa^2 - 1)^2 + 4\kappa^2$ should replace $(\mu^2-1)^2$ in (13).

Our equation has been confined to media possessing only oscillators of one kind. If that limitation be dropped, A and B in equations (8) would have to be replaced by their average value taking account of the difference in the corresponding frequencies. In equation (9) on the other hand we should have to replace $A^2 + B^2$ by its average value. We cannot in this case proceed as before with the elimination of A and B. But when, as in the case of most transparent media, the refractive indices are known to depend on oscillators the periods of which are far removed from that to which the refractive index refers, the error introduced will be small.

We turn our attention next to the absorption which is due to the conversion of the energy of the oscillators into heat. By the influence of molecular encounters or otherwise the amplitudes of the oscillations are reduced until a state of equilibrium is reached. The values of A and B will thus be lowered. If the effect of the degradation of energy is proportional to the energy of the oscillators, we may account for it by applying the factor $(1-f\omega^2)$ to the right-hand side of (10). But if κ is now made to refer to the total extinction of light, we must leave equation (11) as it stands, because the energy which now appears as heat is the exact equivalent of that by which the scattered light is diminished. As a result of the elimination of $A^2 + B^2$ equation (13) now becomes

$$4\pi\kappa\lambda^{-1}(1-f\omega^2) = (\mu^2-1)^2\omega^4/6\pi Nc^4.$$

It should be remembered that $4\pi\kappa\lambda^{-1}$ is the coefficient of the extinction of energy, so that the intensity of the transmitted light is $E = E_0 e^{-4\pi\kappa\lambda^{-1}L}$.

Our equations bring out clearly how erroneous is the common impression that the so-called anomalous refraction is due to the absorption of light in the medium. It is, on the contrary, the perfectly normal result of the changes in refractivity introduced by the excited vibrations of the oscillators: and of the scattering of light which accompanies them. True absorption, *i.e.*, direct conversion into heat, acts, on the contrary, in the direction of diminishing the influence of the molecular oscillations on refractivity. At present we possess no available data to determine the quantity f on which the absorption depends.

On the Effect of Concentration on the Spectra of Luminous Gases.

By T. R. MERTON, M.A., D.Sc., F.R.S., Professor of Spectroscopy in the
University of Oxford.

(Received November 10, 1920.)

It is now more than forty years since Lockyer* made the remarkable observation that in the spectra of electric spark discharges in mixtures of nitrogen and oxygen, the nitrogen lines were narrow and the oxygen lines broad when the oxygen was present in excess, and in the same way the oxygen lines were narrow and the nitrogen lines broad when the nitrogen was in excess. Although Lockyer put this discovery to practical use in order to make accurate measurements of the wave-lengths of the lines, it seems to have been relegated since to the numerous phenomena in spectroscopy which defy an explanation. Effects akin to this are by no means uncommon. It has long been known that the widths of spectrum lines from flames containing sodium or lithium are greatly affected by the concentration of these substances in the flame. Lord Rayleigh† remarks, in connection with the behaviour of the D lines of sodium in the Bunsen flame, "Is there no distinction in kind between encounters first of two sodium atoms and secondly of one sodium atom and an atom, say, of nitrogen? The behaviour of soda flames shows that there is. Otherwise it seems impossible to explain the great effect of relatively very small additions of soda in presence of large quantities of other gases. The phenomena suggest that the failure of the least coloured flames to give so high an interference as is calculated from Doppler's principle may be due to encounters with other gases, but that the rapid falling off when the supply of soda is increased is due to something special. This might be of a quasi-chemical character, *e.g.*, to temporary associations of atoms, or again to vibrators in close proximity putting one another out of tune."

Since these words were written our knowledge of the circumstances which govern the widths of broadened spectrum lines under certain specified conditions has materially increased. Stark's suggestion,‡ that the broadening of the lines in the spectra of condensed spark discharges is intimately connected with the resolution of the lines into components by the electric field, has been fully confirmed, and it has been shown that in the case of hydrogen and helium the broadening observed under these conditions can be accounted for satisfactorily and completely by the resolution of the lines by

* 'Phil. Mag.' [5], vol. 6, p. 161 (1878).

† 'Phil. Mag.' [6], vol. 29, p. 274 (1915).

‡ 'Elektrische Spectralanalyse Chemischer Atome,' 1914.

the electric fields of neighbouring charged particles on the radiating atoms.* The electrical resolution of the lines of hydrogen and helium has been examined by a number of observers, and reliable data, both qualitative and quantitative, are available; in the case of other elements, though considerable progress has been made, our information is less complete, but it is known that for a given electric field the resolution of the lines of heavier atoms such as sodium is very small in comparison with that of the hydrogen or helium lines. It is difficult, therefore, to account for the behaviour of the lines of sodium and many other lines of heavy elements which broaden easily to an extent which seems quite out of proportion to their electrical resolution.

Phenomena depending on the concentration of the radiating atoms are well exhibited in the case of the spectrum of lithium. Lecoq† has shown that the relative intensities of lines of the principal and the subordinate series are greatly affected by the concentration of lithium salt in a solution when the spectrum of sparks from the surface of the solution is examined, the subordinate series being relatively enhanced at higher concentrations. More recently Kouen and Hagenbach‡ and Saunders§ have observed new combination series in the spectrum of lithium in electric arcs in which the concentration of lithium vapour was very great, and King|| has shown that the lithium line $\lambda = 6708 \text{ \AA}$, which in sources containing very little lithium vapour appears as a close doublet, develops a new component when the concentration of lithium in the source is increased. Lockyer's "long lines," which are also the last lines to disappear from the spectrum of a substance when the concentration of that substance in the source is diminished, are another example of the same phenomenon, which thus appears to be perfectly general. Two other phenomena may be mentioned. The pole effect, or the small changes in the wave-lengths of certain lines in the neighbourhood of the poles of the electric arc, has been considered by Royds¶ to be connected with the increase in the concentration of the radiating atoms in this region, and, lastly, Burns** has found that certain manganese lines occurring as impurities in the iron arc differ in wave-length from the lines given by a manganese salt in the carbon arc, some barium lines being affected in the same way. Bilham†† has investi-

* Nicholson and Merton, 'Phil. Trans.,' A, vol. 216, p. 459 (1916); Merton, 'Roy. Soc. Proc.,' A, vol. 92, p. 322 (1916), and vol. 95, p. 30 (1918).

† 'Spectres Lumineux,' p. 56, Paris, 1874.

‡ 'Phys. Zeitschr.,' vol. 4, pp. 592, 801 (1903).

§ 'Astrophys. Journ.,' vol. 20, p. 188 (1904).

|| 'Astrophys. Journ.,' vol. 44, p. 169 (1916).

¶ 'Astrophys. Journ.,' vol. 41, p. 154 (1915).

** 'Comptes Rendus,' vol. 156, p. 1976 (1913).

†† 'Astrophys. Journ.,' vol. 42, p. 469 (1915).

gated a similar case. It thus appears that in certain cases the three phenomena of broadening, variations in the relative intensities of the lines, and changes in wave-length are intimately connected with the concentration of the radiating atoms in the source.

I have carried out a number of experiments with a view to discovering whether the phenomena of broadening and enhancement of certain lines in the case of sodium and lithium can be referred to a quasi-chemical effect in accordance with one of the suggestions of Rayleigh (*loc. cit.*). When the chemical similarity of sodium and lithium are considered, it seems extremely probable that if temporary associations of two sodium atoms or two lithium atoms occur in luminous sources, there will also be temporary associations of sodium atoms with lithium atoms. It would be expected that the addition of a large quantity of lithium to a source containing a small quantity of sodium would result in a broadening of the sodium lines, and similarly the addition of a large quantity of sodium to a source containing very little lithium should broaden the lithium lines, enhance the subordinate series relatively to the principal series, and change the doublet $\lambda = 6708 \text{ \AA.}$ into a triplet. I was unable to obtain a lithium salt sufficiently free from contamination with sodium to examine the effect of the addition of lithium to sources containing sodium, but the converse experiment was carried out without difficulty, both in the case of flames and with arc spectra *in vacuo*. In neither case could any change be detected. With an arc burning between very pure carbon poles, at a pressure of a few millimetres, the phenomena described by King (*loc. cit.*) could be seen clearly when the carbons were treated with dilute solutions of lithium nitrate. The spectrum was observed with a Lummer-Gehrcke plate, crossed with a Hilger constant-deviation spectroscope, and the change of the doublet into a triplet when the quantity of lithium in the source was increased was very striking; but the addition of large quantities of soda produced no such change, nor were the subordinate series enhanced. These experiments seem to exclude temporary associations of atoms, in the chemical sense, as the explanation of the phenomena, but since all the evidence points to a specific influence of atoms of the same kind on one another, it seemed that more decisive results might be obtained from a study of the mutual influence of atoms of hydrogen and helium on one another since in this case we have accurate information of the electrical resolution of the lines.

In the previous investigation,* in which a study was made of the broadening of the lines of helium by condensed discharges, not only were the structures of the broadened lines in complete harmony with their electrical

* Merton, *loc. cit.*, 1918.

resolutions, but a further proof of the existence of powerful electric fields under these conditions was afforded by the presence of the combination series observed by Koch,* and other combination lines which, when the spectrum is excited by uncondensed discharges, are only found in those regions of the discharge tube where the potential gradient is very great. The aforementioned phenomena relating to the effect of the concentration of charged particles lead one to enquire whether, in the broadening of helium lines and hydrogen lines in vacuum tubes, which is definitely due to the electrical resolution, the electric fields which are operative are simply those which are due to the proximity of any charged particles to the radiating atoms, or whether there is something specific in the magnitude of the electrical resolutions produced by the proximity of charged particles of the same kind.

In order to investigate this, a study has been made of the broadening of the helium and hydrogen lines in vacuum tubes containing these gases in varying proportions. The vacuum tubes were of the usual H pattern, and were provided with side tubes, into which were sealed short lengths of platinum tube, connected with palladium tubes, which were closed at the other end; the quantity of hydrogen in the tubes could thus be controlled by heating the palladium tube in a current of hydrogen or in a hydrogen flame, or, alternatively, in an atmosphere free from hydrogen. The most interesting results in the case of helium were obtained with a tube which was filled with helium at a high pressure, the greatest care being taken to exclude impurities; the precise pressure in this tube was not measured, as it was particularly desired to exclude the possibility of contamination with mercury, but, from previous experience and comparison with other tubes in which the pressure had been measured, it may be stated that the pressure was greater than 50 mm. of mercury. The last traces of hydrogen were removed through the palladium tube. The tube was excited by an induction coil with an adjustable spark gap in series, and, by means of a high tension switch, a large condenser could be put in parallel with the terminals of the induction coil. The spectra were observed with a constant-deviation spectro-scope, and photographs were taken with a camera attached to this instrument. With a small spark gap and the condenser in parallel, the lines were found to be enormously broadened, in accordance with their electrical resolution; the Koch (*loc. cit.*) series was strong, and combination lines were observed at $\lambda\lambda$ 6635, 4911, 5043 A., of which the line $\lambda = 5043$ A.† does not appear to have been observed before. These lines, which were measured approximately, were sharp on one edge and diffuse on the other, indicating the

* 'Ann. d. Phys.,' vol. 48, p. 98 (1915).

† Cf. Saunders, *loc. cit.*

unsymmetrical nature of their electrical resolution, but the spark line at $\lambda = 4686 \text{ \AA}$. was not observed with certainty, owing, no doubt, to the fact that the electrical resolution of this line is symmetrical, and it would therefore be so diffuse as to escape notice. On admitting a small trace of hydrogen, the current through the primary of the coil and the length of the spark gap being kept constant, the helium lines were broadened as before, but the hydrogen lines $H\alpha$, $H\beta$, and $H\gamma$ appeared to be perfectly sharp though faint. On further increasing the amount of hydrogen in the tube, the hydrogen lines began to show signs of diffuseness, and, with a large quantity of hydrogen, they became definitely broadened.

These observations were made both side-on and end-on with similar results, excepting that, for a given concentration of hydrogen, the Balmer lines were relatively more intense when the tube was viewed end-on. This follows from Curtis'* observation, that in helium tubes containing a small trace of hydrogen, the Balmer lines could only be detected just outside the capillary, when a condenser and a small spark gap were included in the circuit. For this reason, reliance could not be placed on the end-on observations alone, for in this case the Balmer lines might have their origin just outside the capillary, where the current density would be smaller; but the photographs taken side-on showed the same effect. When discharges of the same intensity were passed through tubes containing pure hydrogen, the Balmer lines were very broad, whilst tubes containing hydrogen and helium in similar proportions gave broadened lines for both elements. The electrical resolution of the diffuse series of helium is less than that of the Balmer lines of equal term-number; thus, using Stark's (*loc. cit.*) results, we should expect the broadening of the line $H\beta$ to be very nearly twice as great as that of the helium line $\lambda = 4471 \text{ \AA}$. The fact that the latter line is broad and $H\beta$ is narrow when the amount of hydrogen present is very small, seems to show that there is in this case a specific action of charged atoms of the same kind on one another, and that the resolution produced by a neighbouring charged atom of the same kind is vastly greater than that produced by a charged atom of another kind. These observations are in agreement with those of Lockyer, but they are made in a case in which there can be little doubt as to the ultimate cause of the broadening.

In repeating Curtis' (*loc. cit.*) observations, which have been referred to above, a very curious fact was noticed. When the high-pressure helium tube containing a little hydrogen was excited by an uncondensed discharge and observed through a direct vision prism, the lines of both hydrogen and helium were of uniform intensity throughout the capillary. On putting in

* 'Roy. Soc. Proc.' A, vol. 89, 146 (1914).

the condenser and a small spark gap, the hydrogen lines became relatively much weaker in the capillary, but showed fairly brightly just at the ends, in accordance with Curtis' observation. When, however, the condenser was cut out again, the hydrogen lines did not immediately reappear in the capillary with uniform brightness, but were seen as bright spots at the ends of the capillary, these bright spots gradually extending until the intensity was uniform, which did not, as a rule, occur until about 30 seconds after the condenser had been cut out. Putting in the condenser for a few seconds only showed the effect to a much smaller extent. The bright spots of the Balmer lines seemed to spread into the capillary in a manner which strongly suggested a diffusion of the gas, and they spread at very much the same rate and with the same general appearance as when a small quantity of hydrogen was let into the tube (previously freed from that gas) whilst the discharge was running. It looks as if the weakening of the Balmer lines in the capillary when the condenser is put in the circuit is due to the fact that the hydrogen is in some way driven out of the capillary into the bulbs by the action of the discharge.

There are many cases in which the relative intensities of the lines in a mixture of two gases is radically altered by the inclusion of a condenser and spark-gap in the electrical circuit. Such phenomena have usually been attributed to the changes in the electrical conditions, but in the light of the observations recorded above it seems by no means improbable that the ultimate cause is sometimes to be found in the alteration of the relative proportions of the gases in the capillary of the discharge tube.

On the Effect of Asymmetry on Wave-length Determinations.

By J. W. NICHOLSON, F.R.S., and T. R. MERTON, F.R.S.

(Received November 16, 1920.)

It is a familiar experience in spectroscopy that the actual accuracy which is attained in precise measurements of wave-length is almost invariably disappointing, and falls far short of the precision to be expected from a consideration of the probable errors. In particular, the measurement of unsymmetrical lines, difficult in itself, is affected by displacements which depend on the limited resolving power of the spectrograph. It is no doubt well known that this effect must be operative, and it has been considered, for example, by Grebe and Bachem* in their search for the Einstein effect in the solar spectrum. But we are not aware of any precise formulation of its magnitude, although a close approximation to the apparent displacement of the maximum of an unsymmetrical line, expressed in the terms of the resolving power and the asymmetry, can be obtained from simple considerations.

We have at present no very precise knowledge of the intensity distribution curves of the unsymmetrical lines which are found in the spectra of the electric arc and of numerous other sources. But we have convinced ourselves, from an inspection of the photometric curves obtained by King and Koch† and St. John and Babcock‡ that for the present purpose, we may assume, without serious error, that the lines may be represented by the purely artificial device of combining two error curves.

We do this by assuming that the intensity falls off from the maximum, on either side of the line, according to the law

$$I \propto e^{-kx^2}.$$

The asymmetry is reproduced by adopting different values of k on the two sides of the maximum.

It is evident that, with infinite resolving power, the positions of the true and apparent maxima will be coincident; but it will at once be seen that, with a finite resolving power, the energy at any point is gathered over a range prescribed, on the usual considerations of wave theory, by the diffraction pattern of the slit. The practical resolving power, however, is affected by other considerations, such as the grain of the plate, and, for

* 'Deutsch. Phys. Gesell. Verh.,' 21, p. 454 (1919).

† 'Astrophys. Journ.,' vol. 39, p. 213 (1914).

‡ *Ibid.*, vol. 42, p. 231 (1914).

practical purposes, we may consider that the light is gathered over a range which is equal to the actual purity of the spectrum. We proceed as follows:—

Consider a line, whose maximum intensity occurs at $x = 0$, which is broadened in the direction of negative values of x according to the intensity distribution law

$$y = e^{-kx^2},$$

and, in the direction of positive values, according to the law

$$y = e^{-k'x^2}.$$

Let the purity of the spectrum be represented by the interval 2ξ , the energy being thus gathered on either side of any point over a range, ξ . Let Q be the abscissa of any point. Then the energy, E , gathered at this point is represented, on the complete graph of the lines, by the area lying above an interval, 2ξ , bisected by the point, Q . Thus

$$E = \int_{-(\xi+Q)}^0 dx e^{-kx^2} + \int_0^{\xi+Q} dx e^{-k'x^2}.$$

It is clear that Q is the value of the displacement required when it is so selected that E is a maximum, or dE/dQ is zero.

Since Q only occurs in the limits of integration, this yields at once

$$-e^{-k(Q-\xi)^2} + e^{-k'(Q+\xi)^2} = 0,$$

or

$$k(Q-\xi)^2 = k'(Q+\xi)^2,$$

whence

$$\frac{Q}{\xi} = \frac{\sqrt{k} - \sqrt{k'}}{\sqrt{k} + \sqrt{k'}} \quad (k > k'),$$

rejecting the value which is obviously inapplicable. Thus the required displacement, Q , is

$$Q = \xi \left(\frac{\sqrt{(k/k')} - 1}{\sqrt{(k/k')} + 1} \right).$$

It is convenient, at this point, to specify the degree of asymmetry in some simple quantitative manner. For this purpose we adopt the ratio of the two "half-widths" of the line on either side of the maximum, these being the values of x which make y equal to $\frac{1}{2}$. They are given by

$$\frac{1}{2} = e^{-kx^2}, \quad \frac{1}{2} = e^{-k'x^2},$$

and calling them x_1 and x_2 , we have

$$\frac{x_1}{x_2} = \sqrt{\frac{k'}{k}}, \quad x_2 = \sqrt{\frac{k}{k'}}.$$

The quotient of the greater value of x by the smaller may be called the

index of asymmetry and denoted by the symbol i . Thus, if $k > k'$, as we assumed above,

$$i = \sqrt{\frac{k}{k'}},$$

and the formula for the displacement reduces to

$$Q = \xi \left(\frac{i-1}{i+1} \right).$$

It is evident that in most spectroscopic measurements, where the accuracy of micrometer settings far transcends the resolving power, this correction is by no means inconsiderable. Thus, on a plate on which lines separated by 0.1 Å. can just be resolved, the apparent displacement in the case of a line whose index of asymmetry is 3 is 0.05 Å, and it is further to be noted that this displacement is independent of the actual values of k and k' . Thus, though a line may be so narrow that no trace of asymmetry can be detected, it may nevertheless show a displacement which might in certain cases lead to entirely wrong conclusions. It is at least possible that some of the difficulties experienced in fitting a formula to a spectrum series may be due to errors arising in this manner. We are thus led to the conclusion that the general practice of measuring wave-lengths to a degree of accuracy far transcending the purity of the spectrum, depends on the assumption that the lines show no serious asymmetry. Whilst the assumption can hardly be accepted generally, it is of interest to note that the above considerations suggest a method of measuring the index of asymmetry in some cases in which the physical width of the line is exceedingly small, for it is evident that, since the displacement can never exceed the purity of the spectrum, a series of measurements made, for example, in different orders of the grating spectrum would afford material for the calculation of the asymmetry. The application of these principles to investigations such as the displacement of lines in the solar spectrum is so evident as to need no further comment.

Magnetism and Atomic Structure.—I.

By A. E. OXLEY, M.A., D.Sc., F.Inst.P., Mackinnon Student of the Royal Society.

(Communicated by Prof. S. Chapman, F.R.S. Received October 6, 1920.)

The present communication aims at an interpretation of the electron structure of matter which is compatible with the results of recent magnetic investigations. While acknowledging in full the success of the Rutherford-Bohr-Sommerfeld theory, in so far as it applies to radiation problems, it must at the same time be admitted that this success is confined to the simplest types of atoms, the hydrogen atom and the positively charged helium atom, each with a single electron, such atoms being very probably in an abnormal state as compared with that which prevails in unexcited matter, and upon which the magnetic determinations have been conducted. As a consequence, we are led to somewhat different interpretations of atomic structure, according to which viewpoint is adopted; but a fuller recognition of the possible differences of atomic structure between radiating and non-radiating matter may, in the near future, enable us to bridge the gap which at the moment unmistakably divides them.

This paper* is a continuation of previous memoirs† on “The Influence of Molecular Constitution and Temperature on Magnetic Susceptibility” (‘Phil. Trans.’ A, vol. 214, p. 109, 1914, Parts I and II; vol. 215, p. 79, 1915, Part III; vol. 220, p. 247, 1920, Part IV; ‘Proc. Roy. Soc.’ A, vol. 95, p. 58, 1918). In Part III, p. 92, and Part IV, pp. 270–276, I have called attention to the classical experiments of Tyndall‡ on the deportment of crystalline bodies in the magnetic field. From observations on about 100 different crystals suspended in a uniform magnetic field, Tyndall showed that, in general, “if the arrangement of the component particles of any body be such as to present different degrees of proximity in different directions, then the line of closest proximity, other circumstances being equal, will be that chosen by the respective forces for the exhibition of their greatest energy. If the mass be magnetic, this line will stand axial; if diamagnetic, equatorial.” Tyndall propounded the “theory of reciprocal induction” to account for the augmented diamagnetic or paramagnetic property in the direction of closest packing of the particles. At that time

* Abstract read before the British Association, Cardiff Meeting, August 27, 1920.

† A *résumé* of these papers is given in ‘Science Progress,’ No. 56, pp. 588–601 (March, 1920).

‡ ‘On Diamagnetism and Magneocrystallic Action,’ p. 23 (1870).

(1870) the diamagnetic forces were known to be so minute that the theory of reciprocal induction, as applied to minute diamagnets, appeared incredible, and, as a correspondence between Lord Kelvin and Tyndall shows,* the former expressed emphatically his opinion that this theory was quite incapable of accounting quantitatively for the effects observed. Regarding a diamagnetic molecule as a simple diamagnet, the mutual actions between such systems would certainly be inadequate. It has, however, been shown (Part II, p. 143; Part III, pp. 83-92) that a diamagnetic molecule is not a simple but a complex diamagnet, formed of at least two components, each of which is strongly magnetic locally. These components are the rotating electrons, whose equivalent magnetic moments are

$$M = \frac{\epsilon S}{\tau},$$

where ϵ is the electronic charge, S/τ the aërial velocity with which the orbit of area S is described in time τ . Since in different types of atoms the electrons are comparable in number, and revolve in orbits for which S and τ are of the same order, the local magnetic fields will be of comparable magnitude whether the atoms be diamagnetic or paramagnetic (see figs. 1a and 1b). Such strong local forces, which are of the order 10^7 gauss,† will account quantitatively, on the theory of reciprocal induction, for the directive effects observed by Tyndall.

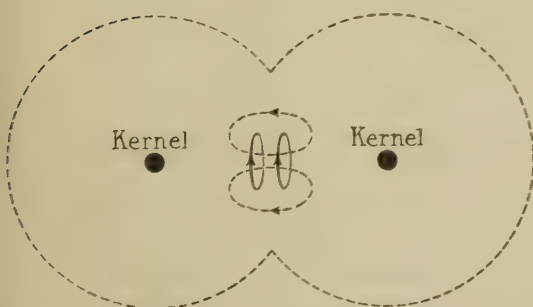


FIG. 1a.—Paramagnetic coupling.

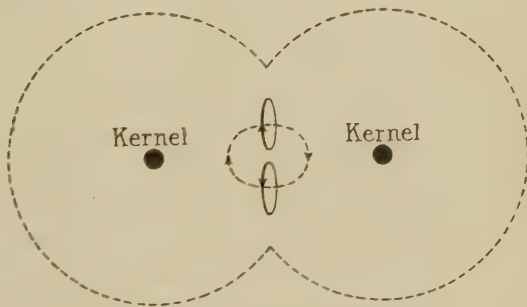


FIG. 1b.—Diamagnetic coupling.

The black dots indicate the diffuse atomic kernels, consisting of positive charges and a spacial distribution of electrons, which are rotating in small circles at varying distances from the nuclei.

In a crystal, the direction of closest packing of the molecules is parallel to the principal cleavage, and, if the remaining cleavages are comparatively insignificant, this direction sets equatorially with respect to the magnetic field if the crystal is diamagnetic, and axially if it is paramagnetic. This is

* *Loc. cit.*, Various Letters, pp. 221-234.

† 'Phil. Trans.' A, vol. 215, pp. 84-87 (1915).

true, within limits, even when the axial dimension of the crystal is greatest in the former case, and the equatorial dimension greatest in the latter case; the diamagnetic crystal thus behaving as regards its outward form like a paramagnetic body, and the paramagnetic crystal like a diamagnetic body. This difference of deportment is shown in fig. 2. In general, other

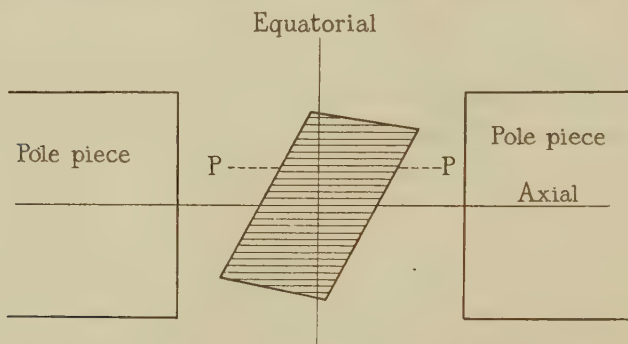


FIG. 2.—Paramagnetic crystal. Direction of principal plane of cleavage, PP, is axial.

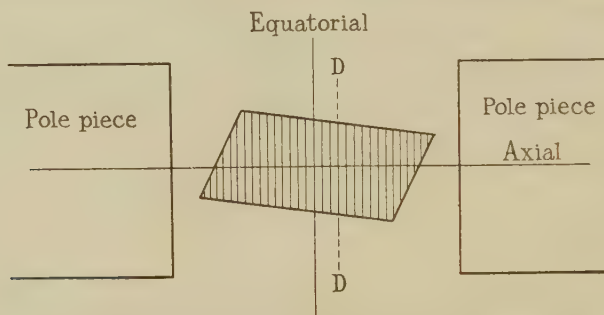


FIG. 2.—Diamagnetic crystal. Direction of principal plane of cleavage, DD, is equatorial.

cleavages than the principal one must be taken into account, and on this Tyndall remarks: "When a crystal cleaves symmetrically in several planes, all parallel to the same straight line, and, at the same time, in a direction perpendicular to this line, then the latter cleavage, if it be more eminent than the former, may be expected to predominate; but, when the cleavages are oblique to each other, the united action of several minor cleavages may be such as to overcome the principal one, or so to modify it that its action is not at all the same as that of a cleavage of the same value unintersected by others."

Recently, I have had an opportunity of extending some of Tyndall's experiments]to the following organic compounds: naphthalene,* anthracene,

* The examination of the deportment of this substance was suggested to me during a conversation with Sir William Bragg, who pointed out its very pronounced cleavage, and I am indebted to Prof. W. L. Bragg for permission to carry out the experimental work in the University of Manchester.

sodium-ammonium racemate, tartaric and citric acids. The effects observed were in agreement with the rules given by Tyndall for other crystalline substances, and it will be sufficient to describe here those obtained with naphthalene, which possesses a very pronounced cleavage. This substance, which is diamagnetic, crystallises in thin plates having monoclinic symmetry. Three piles of these plates were constructed by cementing together selected crystals with Canada balsam (diamagnetic). The numbers of crystal-line plates in the built up specimens were (a) two, (b) forty, (c) about eighty; in (b) and (c), the orientations of the plates, about a direction perpendicular to the principal cleavage, being arranged at random. Each specimen was suspended by a 50-cm. length of unspun silk in a uniform magnetic field of approximately 10,000 gauss. The deportment of each specimen is shown in plan in fig. 3.

The principal plane of cleavage invariably sets itself equatorial, even though in cases (b) and (c) the ratios of the axial to the equatorial dimensions were 1 : 1 and 1.75 : 1 respectively; the specimen (c) thus behaving like a paramagnetic body, in so far as its outward form is concerned, setting its longer dimension from pole to pole. The specimens were diamagnetic, and were definitely repelled from one pole in a non-uniform field. The deportment was in each case decisive, the complete period of oscillation being 10 seconds for specimen (c) with the field off, and 1.5 seconds only with the field on. The specimens could readily be caught with either end opposite the north pole of the electromagnet.

The crystalline structure is evidently so constituted that the diamagnetic effect is a maximum parallel to the principal cleavage, and in this direction also the cohesive force is a maximum. I have, in a previous paper,* attributed this cohesive force to the mutual induction between a pair of electron orbits, for it appears that, in organic compounds where there is no

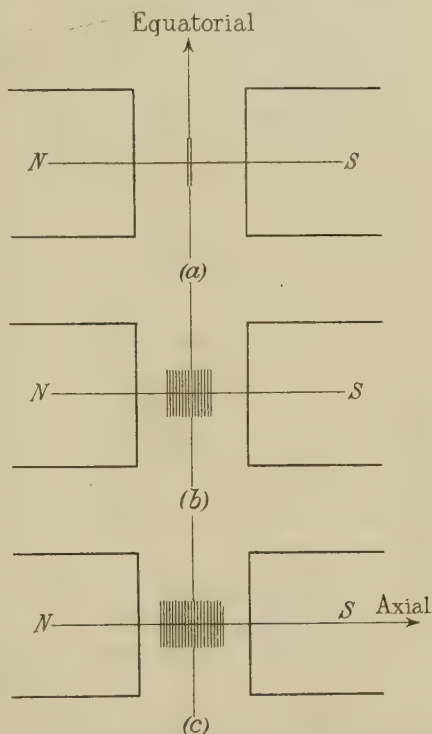


FIG. 3.—Deportment of naphthalene crystals in magnetic field. (Plan.)

* 'Phil. Trans.,' A, vol. 215, p. 83 (1915).

ionisation, and in elements composed of identical particles, it is only by such means that attraction can be secured at all (unless one assumes the existence of some hypothetical constitutive force whose origin is entirely unknown and consequently does not help us).

The coupling is of the nature shown in figs. 1*a* and 1*b*, the latter type of coupling being necessary in the case of the hydrogen molecule, containing only two electrons, in order to preserve its diamagnetism. A suggested model of the hydrogen molecule* is illustrated in fig. 4. The pair of electrons,

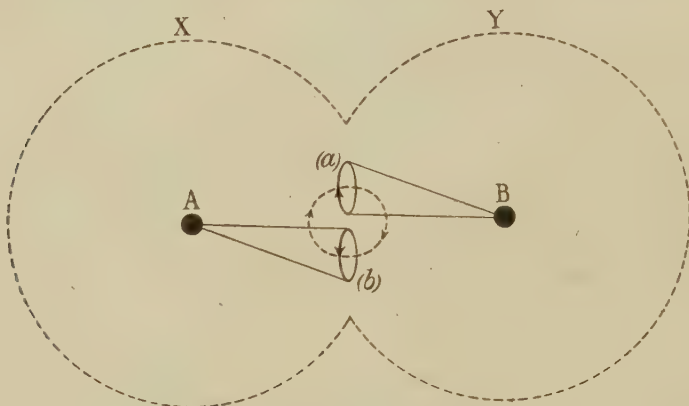


FIG. 4.—Model of hydrogen molecule.

a and *b*, held in common by two exactly similar atoms, X and Y, constitute an astatic system, each electron revolving in a small circular orbit (or

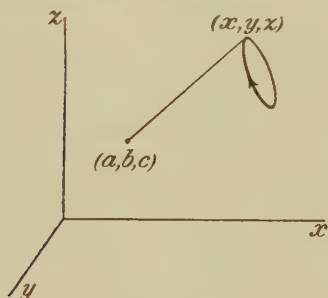


FIG. 5.

possibly an ellipse) and being completely, or more probably almost completely, bound to its own nucleus by a tube of force.† The equilibrium of the electron orbits is one in which a balance is secured between the residual electrostatic repulsive forces and the magnetic attractive forces.‡

As regards the deportment of an unsymmetrical diamagnetic atom in a magnetic field, let *x*, *y*, *z* be the co-ordinates of an electron,

* A. E. Oxley, 'Nature,' vol. 105, pp. 327–328 (May 13, 1920).

† It will be observed that each hydrogen atom will, on this view, be paramagnetic. The ferromagnetism of manganese (Sir Robert Hadfield, Chéneveau, and Généau, 'Roy. Soc. Proc.,' A, vol. 94, p. 65 (1917)), fused in an atmosphere of hydrogen, may possibly be attributed to occluded hydrogen in the atomic state. It is an interesting fact that hydrogen is readily occluded by other highly magnetic elements.

‡ Cf. 'Phil. Trans.,' A, vol. 220, p. 289 (1920).

a, b, c those of the nucleus or centre of gravity of the atom (fig. 5).
Writing

$$(\xi, \eta, \zeta) = (x-a, y-b, z-c),$$

then the induced diamagnetic moment, ΔM_z , due to the application of an external field H_z parallel to O_z is

$$\Delta M_z = -\frac{e^2 \cdot H_z \cdot A}{4m}, * \quad (1)$$

where

$$A/2 = \Sigma \xi^2 = \Sigma \eta^2 = \Sigma \zeta^2$$

and e/m is the ratio of the charge to the mass of an electron. This holds for any type of orbit. If the orbit is in a plane parallel to H_z , ΔM_z is zero; for any other orientation of the orbit, ΔM_z is negative, whatever the direction of revolution of the electrons, because (1) does not depend on the angular velocity. In the case of a diamagnetic coupling system like that shown in fig. 1*b*, the pair of orbits would tend to set with their common plane parallel to the magnetic field. In a crystal, each molecule, except for small thermal oscillations, presents a constant orientation to its neighbours, and the cohesive or coupling forces will in general be stronger in some directions than in others. Thus, in the case of the diamagnetic naphthalene crystals, providing the electron coupling is strongest in a direction parallel to the principal plane of cleavage, due to a closer interaction between molecules which lie in a line parallel to this plane, we should expect the planes of these coupling orbits to set axially, *i.e.*, the plane of cleavage should set equatorially, as it actually does. Any departure from this setting would produce an increased diamagnetic effect, causing the crystal to return to the equatorial position, which is therefore stable. In general there will be structural forces in other directions, but where the principal cleavage is so pronounced, as it is in naphthalene, the deportment of the crystal in the magnetic field will isolate the principal cleavage.

On the other hand, in paramagnetic crystals, where the principal cleavage is determined by a paramagnetic pair of coupling orbits, as shown in fig. 1*a* this cleavage will set axially with respect to the magnetic field. Any displacement from this position results in an increase of potential energy and therefore this position of equilibrium is also stable.

In other words, both in diamagnetic and paramagnetic media, the planes of the electron orbits have a greater aggregate projection perpendicular to the principal cleavage than parallel to it. As a consequence, the existence of several cleavages, even though they be minor ones, demands a spacial distribution of electron orbits about the atomic nuclei.

* 'Phil. Trans.,' A, vol. 214, p. 137 (1914); and references to Langevin's paper there given.

It appears from these considerations that, except perhaps for crystals of compounds of the simple cubic form, it is possible to isolate the fundamental unit of the crystal structure by observing the equilibrium positions of a crystal when suspended in different ways in a magnetic field. These equilibrium positions are consistent with the disposition of the planes of cleavage, *i.e.*, with the closer or more open packing of the molecules in certain directions. In such cases *the fundamental unit of the crystal structure is the molecule*.*

Recently, the existence of special relationships between pairs of electrons has been supplied by X-ray work,† but it seems doubtful if definite evidence as to the nature of the electron coupling can be safely drawn from this source until the effects of thermal oscillations on the intensity of the diffraction effects have been investigated.

In a simple cubic crystal like rock-salt, the X-ray analysis indicates that all the atoms of one kind are equally influenced by their symmetrically disposed neighbours.‡ It is interesting to note that rock-salt shows no appreciable structural deformation in the magnetic field, the evidence of three equally important cleavages at right angles to one another satisfactorily accounting for this.

The views on atomic structure which have been given above are consistent with the theory of the cubical atom first suggested by G. N. Lewis§ and

* Cf. 'Phil. Trans.,' A, vol. 220, p. 274 (1920); 'Science Progress,' No. 56, p. 596 (1920).

† Debye and Scherrer ('Phys. Zeits.,' vol. 18, p. 291 (1917)) have examined the structure of graphite, and from their results, W. L. Bragg ('Phil. Mag.,' vol. 40, p. 185 (1920)), has suggested that certain of the atoms are sharing electrons. In a later paper, Debye and Scherrer ('Phys. Zeits.,' vol. 19, p. 47 (1918)) have considered the structure of diamond and consider that such pairs of coupling orbits are inconsistent with the experimental work of the Braggs. This conclusion is criticised by D. Coster ('K. Akad. Wetensch. Amsterdam,' vol. 22, p. 1 (1919)), who points out that if the different orientations of the planes of the coupling orbits are taken into account, it is impossible in the present experimental stage to draw any definite conclusions from the X-ray diffraction experiments as to the nature or existence of the coupling electrons. James and Tunstall ('Phil. Mag.,' vol. 40, p. 239 (1920)) show that in antimony, the planes of atoms are disposed in pairs. Taking the close pair, and one atom in each, the nearest distance between atomic centres is $2.87 \text{ \AA.U.}$ Taking the wide pair, the corresponding nearest distance is $3.37 \text{ \AA.U.}$ They remark that the very good cleavage of antimony is parallel to these pairs of planes. Antimony possesses other cleavages, and it is possible that similar, though smaller, differences of atomic distances exist for these minor cleavages, and, if so, we may expect direct evidence of the isolation of the molecule in crystalline antimony.

‡ Cf., however, Thirring, 'Phys. Zeits.,' vol. 21, p. 281 (1920), in connection with the crystal lattices of rock salt and sylvine. Thirring introduces magnetic forces to account for the hemihedrism of sylvine.

§ 'J. Amer. Chem. Soc.,' vol. 38, p. 72 (1916).

afterwards considerably extended by Irving Langmuir.* This theory presents certain analogies to Bohr's theory, but differs from the latter in respect of a spacial distribution of the electrons about the nucleus. The electrons must, however, be rotating;† possibly in small circles or ellipses at various distances from the nucleus, in order to account for permanent magnetism and optical activity,‡ as suggested in previous work. Alternatively, the electron itself may be a complex unit endowed with specific magnetic as well as electrostatic properties; this would be equivalent magnetically to a revolving electron and might in some respects be more satisfactory. In either case, during the process of radiation, the electron passes discontinuously through a series of states; the positions of equilibrium, viz., those defining the normal atom, being spherical or ellipsoidal surfaces on each of which the electrons form a space pattern. This would be the three-dimensional interpretation of the mechanism of radiation suggested by Bohr's theory.

According to the Lewis-Langmuir theory, the most stable electron grouping, in elements and in compounds of the electro-negative elements, is a pair of electrons. The next most stable arrangement is the octet, *i.e.*, eight electrons arranged at the corners of a cube. This cube is often very much distorted, and "when a pair of electrons is held in common between two atoms, the chemical evidence indicates that the pair acts as a unit." Such a pair constitutes the single valency bond.§ Lewis's arguments for the close approach of the electrons in the pair, which we have attributed to magnetic induction, are based upon a discussion of:—(1) The origin of the triple bond, due to the pairing of the eight electrons of the octet so as to form a tetrahedron; (2) The interpretation of the Baeyer strain theory; (3) The explanation of the free mobility about a single bond which must always be assumed in stereo-chemistry.

The cubical atom theory gives us a much clearer picture of the nature of diamagnetism and paramagnetism than the Bohr-Sommerfeld theory, with its large unbalanced electron orbits, can give at present, and it appears that a similar remark applies to the interpretation of crystal structure.|| Born and Landé¶ have studied the compressibilities of the alkali halides, on Bohr's assumptions, and conclude that the electron orbits do not lie in a plane, but

* *Loc. cit.*, vol. 41, p. 868 (1919).

† 'Phil. Trans.,' A, vol. 220, pp. 274, 289 (1920); A, vol. 215, p. 87 (1915). 'Nature,' vol. 105, p. 105 (1920).

‡ W. E. Garner, 'Nature,' vol. 104, p. 661 (1920); vol. 105, p. 171 (1920).

§ Cf. 'Phil. Trans.,' A, vol. 220, pp. 277-280 (1920).

|| W. L. Bragg, 'Phil. Mag.,' vol. 40, p. 169 (1920).

¶ 'Verh. Deutsch. Phys. Gesell.,' vol. 20, pp. 210, 230 (1918).

are arranged in space with cubic symmetry.* Sommerfeld also expresses the view that such a conception may eventually enable us to overcome certain outstanding difficulties connected with spectra.

Magneocrystallic action, as we have seen, demands a spacial distribution of electron orbits. All diamagnetic substances (and these form by far the larger proportion of substances known to us) must be internally self-compensated. This may be secured by a symmetrical distribution of electron orbits.

Paramagnetic molecules, in general, have unbalanced magnetic moments. This does not imply that on crystallisation ferro-magnetism would result. On the lines of the cubic atom theory, it is easy to extend Ewing's model to atom groups of eight elementary magnets, each of which has a definite resultant moment, and to arrange systems of such groups so that the crystalline aggregate possesses a zero magnetic moment in the absence of an external field. When a field is applied, a re-distribution of the resultant magnetic axes of the groups will take place, accompanied by the appearance of paramagnetism, which may be different along specialised directions and which will depend upon the temperature.

Ferro-magnetism is a limiting case, depending on a crystalline molecular grouping, which is unstable for fields above a certain strength, and in which, when this field strength has been reached, saturation and permanent magnetisation are produced, either by a rotation of certain molecules as a whole, or by a rotation of the planes of individual electron orbits in those molecules.

On the views which have been expressed above, the rigidity of crystalline media is due to the highly localised nature of the small magnetic coupling elements. A relative rotation of the two coupling circuits through an angle comparable with 45° would so weaken the coupling, due to the transverse separation of the minute magnetic doublets, that the crystalline cohesion would disappear. Consequently, a sufficient rise of temperature to cause such oscillations would result in fusion, the isotropic liquid produced having no rigidity. Such oscillations would have very little effect on the electrostatic stress between the molecules, since the electrostatic doublets are comparable in length with atomic dimensions. It is suggested that the Laplace intrinsic pressure is due to this electrostatic stress. Crystallisation is accompanied by a directed magnetic stress, which, superimposed upon the Laplace pressure, gives rise to a crystalline symmetry characteristic of the molecular configuration. The rigidity of isotropic gels, as pointed out in 'Phil. Trans. Roy. Soc.,' A, vol. 215, p. 81, 1915, is of a different nature, and

* 'Atombau u. Spectrallinien,' 1919, p. 368.

is due to an interlocking of molecules, whose axes are arranged at random, when the thermal agitation is sufficiently and quickly reduced.

Conclusions.

The close relationship which exists between the equilibrium positions of diamagnetic and paramagnetic crystalline bodies, suspended in a magnetic field, and the directions of the cleavage planes can be satisfactorily interpreted in terms of a spacial distribution of electron orbits round the nucleus. The orbits may have any shape, but are probably small in comparison with atomic dimensions. In un-ionised media there is evidence that the coupling force between the units of the crystalline structure is that of magnetic induction; the mechanical stress accompanying it being balanced by the stress due to the distortion of the internal electrostatic configuration of the units. The coupling systems, which account for these attractions, are pairs of electron orbits. In this respect the present theory is closely allied to the cubical atom theory of Lewis and Langmuir, in which the most stable electron arrangement is that of a pair.

Tyndall's discovery relating to the characteristic deportment of diamagnetic and paramagnetic bodies in the magnetic field has been confirmed for a few organic compounds, and the interpretation of the results on the electron theory implies that, both in diamagnetic and paramagnetic crystals, the planes of the electron orbits have a greater aggregate projection perpendicular to the principal cleavage than parallel to it. Thus the existence of multiple cleavages demands a spacial distribution of electron orbits. Moreover, as the molecules are closest packed in a direction parallel to the principal cleavage, the isolation of all the cleavages by suitably suspending the crystal in a magnetic field really isolates the unit of the crystal structure. This unit is the chemical molecule. It is interesting to note that crystals of the simple cubic form, for which X-ray analysis indicates an ionised atomic structure, rather than a molecular structure, show no appreciable structural deportment in the magnetic field.

It is probable that the atoms of hydrogen and helium, the structure of which has been so successfully attacked from the radiation standpoint by Bohr and Sommerfeld, are, when radiating, in a state very different from the unexcited matter upon which magnetic observations have been made. In magnetic work we are concerned with matter in what we may call the "normal state," each atom of which contains at least one electron within the active range of another electron in an adjacent atom, and the mutual interaction of such systems must be taken into account. Some factor seems to have been neglected in Bohr's theory, which, though of small importance

when the atoms contain each only one electron and are independent of each other, yet is of primary importance for matter in its normal state, and without which it is impossible to explain either the magnetic properties of crystals or crystal structure. The attraction between exactly similar atoms, the directed valencies required by stereo-chemistry, and the directive forces within crystals are explicable only by a due recognition of the magnetic force in material media.

It is probable that the Laplace intrinsic pressure in liquids and in isotropic gels is due to electrostatic doublets of atomic dimensions. When crystallisation sets in, superimposed upon the electrostatic stresses, are the directional stresses due to the magnetic doublets which, for a given molecule, determine a characteristic crystalline symmetry, and, owing to their highly localised nature compared with the electrostatic doublets, determine the rigidity of the crystal. Such highly localised magnetic doublets suggest either that the conventional electron is moving in an orbit very small compared with atomic dimensions, or else that the electron itself is a complex unit endowed with specific magnetic as well as electrostatic properties, *i.e.*, the electron is also a magneton (*supra*, p. 271).

*On the Measurement of Low Magnetic Susceptibility by an
Instrument of New Type.*

By ERNEST WILSON, M.Inst.C.E., M.Inst.E.E.

(Communicated by Prof. J. W. Nicholson, F.R.S. Received November 5, 1920.)

It is well known in instruments of the Curie type that when the magnetising force impressed upon the substance is varied and the mechanical force is balanced against that of the torsion in a suspending fibre, the deflections follow the square law and the range through which the magnetic force can be varied is restricted. In fact, it is difficult with the Curie balance to measure the susceptibility of a given specimen outside a narrow range of magnetic force of about one to five. One object in the design of the present instrument was to be able to measure susceptibility with a given specimen through a wide range of magnetic force. Another object was to make the instrument portable in the sense that no spot of light and scale are required, and yet be able to measure susceptibility through a wide range. In all the tests so far made the instrument was placed on an ordinary table.

The fundamental idea is to replace the force due to torsion in a suspending fibre by either an electro-magnetic or electro-static system in which the mechanical force is due to two components—one proportional to the magnetic force impressed upon the specimen, and the other also proportional to the magnetic force in the case of constant susceptibility, but variable if the susceptibility varies. In the electro-magnetic case a moving coil can be employed, which is suspended in a magnetic field proportional in strength to the magnetic force acting upon the specimen. This is the method adopted in the present paper. It has the advantage that the absolute value of the susceptibility can be calculated from the known details of the instrument, and a considerable mechanical force can be produced. In the electro-static method we are concerned with the product of two voltages—one proportional to the magnetic force acting upon the specimen, and the other also proportional to this force if the susceptibility is constant, but otherwise varying with the susceptibility. This method has the advantage that the suspending fibre has only to carry a charge to the moving system, and not a definite current as in the electro-magnetic system. Also there is no question as to magnetic disturbance due to stray fields.

I. Description of the Instrument and Apparatus.

The electro-magnet, *M* (fig. 1), which produces the magnetic field in which the specimen to be tested is suspended, is capable of motion to and fro on brass rails 1, 1, of circular section. The movement is controlled by a screw, 2, which is turned by hand. The winding of the electro-magnet, *M*, is continued by flexible conductors to terminals, 3, fixed on the base of the instrument. The electro-magnet, *M*₁, which supplies the magnetic field for the moving coil, 5, is mounted on the elevated base, 4, and supported on brass pillars, 6, and its winding is connected to terminals, 7. The suspending fibre, 8, which supports the moving coil, is attached to a torsion head, 9, which also allows of an up-and-down movement for taking the moving system on and off suspension. The specimen, 10, is supported in a grip which hangs from the extremity of a beam, 11, made of aluminium wire, 0.32 cm. diameter.

The beam is rigidly fixed to the moving coil and the specimen is counter-weighted by a sliding weight, 12. The horizontal distance between the centre of suspension and the centre of the specimen is 11 cm., which is therefore the effective radius. A scale, 13, fixed to the framework of the instrument, allows of any angular displacement from the true zero position being noted. As an aid to accuracy the beam is fitted with fore and back sights, 14, 15. The torsion head is carried by a horizontal brass plate, 16,

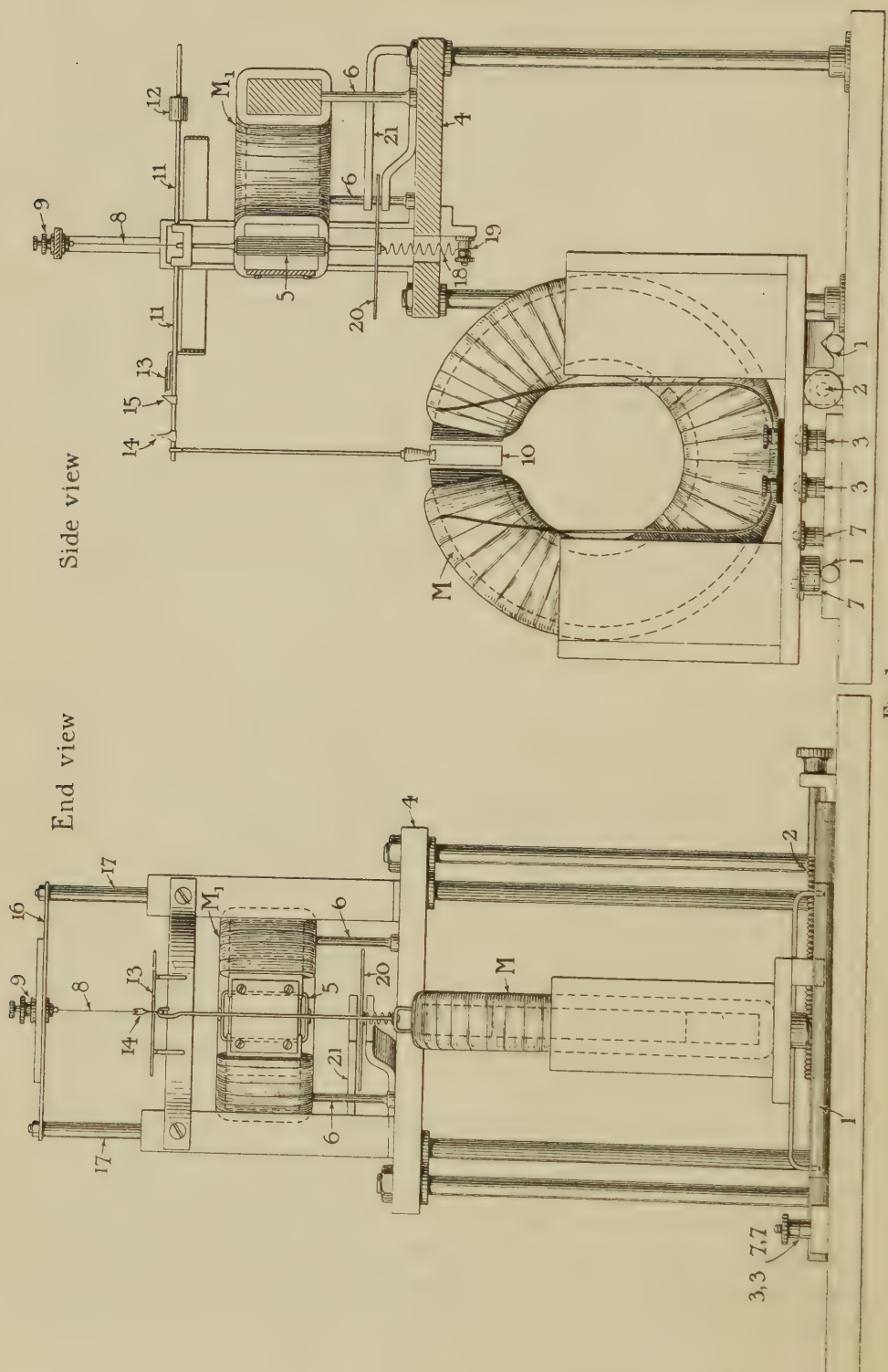


FIG. 1.

supported at each end by pillars, 17. The current in the moving coil is carried by a conductor to the lower portion of the torsion head, 9, and passes down the suspending fibre through the coil and out by means of a spiral, 18, attached to the terminal, 19. A disc of aluminium, 20, whose diameter is 7.5 cm., is supported on an extension of the axis of the moving coil, and is free to move between the poles of a permanent damping magnet, 21. As a protection against draught, the instrument was covered by a glass shade.

A diagram of the connections is given in fig. 2, in which M and M_1 are the

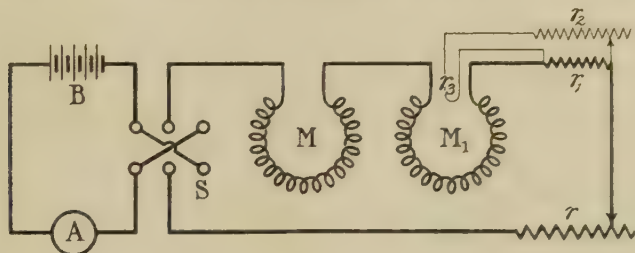


FIG. 2.

windings of the electro-magnets, placed in series with one another and with a shunt resistance, r_1 , across which are connected an adjustable resistance, r_2 , and the moving coil, r_3 . In general, the current in the coil M is equal to that in M_1 , as shown in fig. 2. On some occasions, however, the coil M was shunted, thus reducing the current through it. For this reason the currents in M , M_1 are represented by the symbols A , A_1 respectively. The current in the circuit is measured by the ampèremeter, A , and adjusted by means of a variable resistance, r . The current is supplied by a battery, B , and its direction through the magnet windings, M , M_1 can be reversed by the switch, S , a necessary precaution when the effects due to residual magnetism have to be removed.

II. The Main Magnet.

The magnet, M (fig. 1), is the same as was used in connection with the measurement of the susceptibilities of various kinds of rock specimens,* and it is not necessary to describe it in great detail. The core is in the form of a ring of Stalloy, of rectangular section, which has an outside diameter of 18 cm. and an inside diameter of 10.5 cm. Its thickness is 1.6 cm. A radial air-space with parallel sides is cut in the ring and the width is 1.5 cm. The poles are tapered at an angle of 60° with the plane of the ring, and the opposing faces are 1 cm. wide. The winding on the ring consists of 837 turns

* 'Phil. Trans.,' A, vol. 219 (Appendix, 1919), pp. 83-87; 'Roy. Soc. Proc.,' A, vol. 96, p. 429 (1920).

in four layers of copper wire, 0.122 cm. diameter, insulated with two layers of cotton.

Exhaustive experiments were made to determine the distribution of the magnetic field in the air-space in a direction at right-angles to the plane of the ring, and therefrom the values of $\partial H^2/\partial x$, the gradient of the square of the magnetic force, were obtained for various currents in the magnetising coil. Further information on this subject can be obtained on reference to the original paper.

III. *The Moving Coil Magnet.*

The magnet, M_1 (fig. 1), has a core of wrought iron of rectangular section and 4 cm. deep. Its external diameter is 10 cm. and its internal diameter is 6 cm. It is wound with copper wire, 0.122 cm. diameter, doubly insulated with cotton in four layers, having a total of 301 turns. A circular air-space is cut in the ring, 2.85 cm. diameter, whose axis is parallel with the main axis of the ring. A wrought-iron cylinder, 2.35 cm. diameter and 3.25 cm. long, is supported symmetrically with the air-space by a brass plate, which bridges across the outside of the air-space. These dimensions are suitable for the insertion of a standard Weston moving coil, which was kindly given to the author by the Weston Instrument Company for the purpose of these experiments. The diameter inside the aluminium former on which the coil is wound is 2.5 cm., and the diameter over the winding is 2.66 cm. The estimated mean diameter of the winding is 2.62 cm. Effectively the turns are eighteen, and consist of two windings in parallel, each of which has eighteen turns. The resistance of the coil is 1.14 ohms.

Preliminary experiments were made with a search coil in the air-space and a ballistic galvanometer, to determine the relation between the magnetic force, H_1 , and the current, A_1 , in ampères in the magnetising coil. Unfortunately, for currents up to 1 ampère, the resulting curve is not a straight line, and the ring is evidently not of the best grade of annealed wrought iron. For this reason, a more elaborate treatment than is outlined in the fundamental theory has been found necessary. Had it been available, the author would have liked a ring of Stalloy, which would have given practically a straight line within the limits of the magnetising currents adopted. The relation between the magnetic force, H_1 , and the ampères, A_1 , is as follows, and has been taken from the mean curve:—

Ampères A_1	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Magnetic force H_1	40	93	153	222	290	360	427	497	566	635

IV. Fundamental Theory.

The relation between the magnetic force, H , in the air-space of the magnet, M , and the magnetising current, A , is very closely a straight line. Let the current in ampères be denoted by A , then $H \propto A$. H is also a function of x , the distance measured at right-angles to the plane of the magnet ring. Let this function be denoted by $f(x)$. We have then $H = qAf(x)$, where q depends neither on the ampères, A , nor the distance, x . Then, if K is the susceptibility and V is the volume of the body, the mechanical force, F , exerted by the magnetic field upon the specimen, is given by

$$F = \frac{1}{2}KVq^2A^2\frac{d}{dx}f^2(x).$$

Therefore for any given distance $F \propto A^2$.

If the intensity of the magnetic field for a given current in the moving coil magnet, M_1 , is constant and equal to H_1 , then the mechanical force in dynes, which is produced at the radius of the moving coil, is equal to $2H_1lan$; where l is the length of a single conductor, a is the current in the conductor in C.G.S. units, and n is the number of conductors. If R is the radius of the beam which supports the specimen, and r is the radius of the moving coil, the force, F , is, when a balance is obtained, equal to $2H_1lanr/R$.

The current, a , in the moving coil (fig. 2) is equal to $Ar_1/r_1+r_2+r_3$, and, since r_1 is a constant, $a \propto A/r_1+r_2+r_3$. If the force, H_1 , is proportional to the magnetising current, A , the force, $F \propto Aa$, that is, it is proportional to $A^2/r_1+r_2+r_3$. But F is also proportional to KVA^2 . Therefore the susceptibility, K , per unit volume is proportional to $1/r_1+r_2+r_3$, or it is equal to $C/r_1+r_2+r_3$, where C is a constant. The determination of this constant is naturally the fundamental problem for any instrument constructed after this pattern.

V. The Torque Exerted by the Moving Coil.

For a given current in the magnetising coil of the magnet, M_1 , it was necessary to find the relation between the torque exerted by the coil when a known current was passed through it. Since the magnetic force, H_1 , in the air-space is known in terms of the magnetising current, it should be possible to calculate the torque from the equation

$$T = H_1 a \left(\frac{2lnr}{10} \right) k;$$

where H_1 is the magnetic force, a the current in ampères, l the length of a single conductor, n the number of conductors, r the mean radius, and k is a coefficient to correct for fringing. T is the turning moment measured in

dyne-centimetres. From the particulars already given, $l = 3.25$, $n = 18$, $r = 1.31$, the dyne-centimetres are equal to $1.39 H_1 a k$.

A phosphor-bronze strip, 10 cm. long, and having a rectangular cross-section, 0.85 mm. $\times$ 0.09 mm., was used temporarily as a suspension for the moving coil. This strip had been previously tested, and is the same as used in the balance already alluded to (*loc. cit.*). It requires 1.51 dynes at a radius of 10.9 cm. to twist it through 1° . As used in the present instrument, the moving coil always occupies the position of zero torsion in the suspending fibre when the force exerted by the magnet, M , upon the specimen is a maximum; the adjustment being made by a movement of the magnet on the slide rails. It was therefore necessary to first deflect the coil by turning the torsion-head, and then to adjust the current, a , until it was brought back to zero position. The large angular deflections were read on the instrument scale, and for small angles, a spot of light from a mirror was used. The force in dynes is that exerted at 11 cm., the radius adopted in the instrument. As was to be expected, the ratio (dynes)/ $A_1 a$ is not constant, but experiment shows that, for a given value of the current, A_1 , the ratio is also a function of a . It is therefore necessary to define the limiting values of a for given values of the ratio and magnetising current, A_1 . Wider limits can be adopted when the current, A_1 , is large than when it is small. By plotting the ratio (dynes)/ $A_1 a$, in terms of A_1 , the value of the ratio for any given value of A_1 can be found. This method eliminates all errors due to the taking of dimensions and the counting of turns, and it allows of an accurate determination of the coefficient, k , in the expression for the torque above given. The values of k are not constant, but vary as follows:—

Magnetic force H_1	609	130	47	16
Values of k	1.14	1.24	1.3	1.6
Maximum values of a	0.004	0.01	0.017	0.025

VI. *The Suspending Strip.*

In the early stages of these experiments a silver strip having a resistance of 0.051 ohm per cm. was employed for suspending the moving system, and a spiral of the same strip was used to conduct the current from the moving coil. The suspending strip had a length of 5.2 cm., and the resistance of the complete moving coil system was 3.2 ohms. A length of 10 cm. of this strip requires 0.0131 dyne-cm. to produce a twist of 1° . Latterly a phosphor-bronze strip has been used for suspension 7.9 cm. long, which requires 0.00505 dyne-cm. to produce 1° of twist in a length of 10 cm. The resistance of the complete moving coil in this case is 13.73 ohms.

VII. *The Instrumental Constant.*

Exhaustive tests were made with the magnet, *M* (fig. 1) in order to establish the relation between the square of the magnetising current in amperes (A^2) and the force required to just remove a suspended specimen from the magnetic field against the force of torsion in a phosphor-bronze strip. It was found from the instrument itself as the mean of several determinations that the mass-susceptibility was equal to $93.6 \times 10^{-9} \theta / A^2 m$; where θ was the observed deflection and m was the mass of the specimen. The mechanical force in dynes per degree of twist at a radius of 10.9 cm. was 1.51, and the angle corresponding to unit value of θ was 0.0093 degree: so the total mechanical force was $1.51 \times 0.0093 = 0.0141$ in this instance. The ratio $93.6 \times 10^{-9} / 0.0141 = 6.64 \times 10^{-6}$ is the constant to be used when θ is eliminated, assuming equal radii, and the expression for K_m becomes dynes $\times 6.64 \times 10^{-6} / A^2 m$. In the fundamental theory the force in dynes exerted by the moving coil is assumed to be a constant multiple of $A_1 \alpha$. For reasons already given this is not the case in the present instrument. This constant which we may call *C*, after careful determination has been plotted in terms of A_1 , and from this curve the values used in the calculations have been obtained. The values of *C* ranged from 697×10^{-6} when the current A_1 had the value 0.0739 to 1060×10^{-6} when the current A_1 was 0.970 ampère. We have, therefore, $K_m = A_1 C 6.64 \times 10^{-6} / A^2 m$ as the final expression for the mass-susceptibility.

VIII.

Manganese Sulphate.—Certain materials had to be chosen with which to test the instrument over a wide range of magnetic force, and as manganese sulphate had proved itself to be a most reliable and constant substance it was used in the first instance. The values given in the Landolt-Börnstein (1912) Tables for the mass-susceptibility (K_m) of manganese sulphate are (98, 114, 100, 85) 10^{-6} C.G.S. unit. The variation among these values is considerable, and the mean of the four is 99×10^{-6} . A glass tube containing 1.7 gm. of anhydrous manganese sulphate was tested with the magnet, *M* (fig. 1) using the torsion in the phosphor-bronze strip alluded to, and the value of the mass-susceptibility was found to be 0.001 very nearly.

In the first test made with the above sample of anhydrous manganese sulphate, the connections were as shown in fig. 2, and the resistance of the shunt r_1 was 2.409 ohms. As it was necessary to discover if the moving coil magnet, M_1 , had any disturbing effects on the field due to the magnet, *M*, the currents in the moving coil and its magnet winding were reversed relatively to the current in the magnet winding of *M*. This change was made when the current, *A*, had reached the value 0.96 ampère. Assuming the susceptibility

of the sulphate to be constant the values of $r_1 + r_2 + r_3$ should, on the theory, be also constant. For reasons already given this is not the case, and the values are now given in terms of the magnetising currents, A_1 .

$A_1 = A \dots$	0.26	0.36	0.513	0.727	0.96	0.953	0.74
$r_1 + r_2 + r_3$	83.6	86.6	90.6	95.3	98.6	100.6	97.6

$A_1 = A \dots$	0.523	0.37	0.26	0.143	0.113	0.086	0.0373
$r_1 + r_2 + r_3$	92.6	87.6	83.6	75.6	74.1	72.6	70

In all fourteen measurements were recorded: H was varied from 25 to 642 C.G.S. units, and the corresponding change in K_m was about 11 per cent. The average value of K_m was 94.2×10^{-6} . The damping magnet was turned over to see if this had any serious effect upon the results—none was discovered.

In another series of experiments the current in the moving coil magnet winding was maintained constant during each test in which the current in the main magnet, M , was varied. Taking an average in each case the values of K_m vary as follows:—

Ampères in moving coil magnet winding A_1	0.208	0.393	0.633	1.03
K_m	90	91.1	92.4	96×10^{-6}

The mean of these final results is 92.4×10^{-6} .

The best working range for the current in the winding of the moving coil magnet is 0.1 to 1.0 ampère. As already stated, the currents in the magnet windings of the magnets, M , M_1 , are not always equal in any one test. In the case of the higher susceptibilities a shunt to the magnet, M , has been employed in order that the magnet, M_1 , may be working within its best range.

Chrome Alum (2.47 gm.).—The mass-susceptibility of chrome alum was found to be 0.000014 with a force $H = 468$ when tested against the torsion of the phosphor-bronze strip. Tested in the present instrument over a range of H from 49 to 717, its value varies from 0.0000137 to 0.0000130. This substance is a valuable sub-standard when susceptibilities of small order are in question.

Iron Pyrites (5.57 gm.).—As an illustration of the measurement of low susceptibility some cubic iron pyrites was tested in powder form, and gave values of K_m varying from 0.99 to 0.979×10^{-6} over a range of H of 168 to 740. When tested against the phosphor-bronze strip a value of 1.5×10^{-6} was found for this variety.

Kenytite (from Cape Evans, Ross Island).—This substance is of interest in connection with the scientific work of Scott's Antarctic Expedition, 1910–1913, and the sample tested was kindly sent to the author by Dr. C. S. Wright, of the Admiralty Department of Scientific Research and Experiment. Unlike Franklinite and green serpentine which have susceptibilities of the same order of magnitude, and which like some grades of magnetite (Manchurian for example*) require a very large magnetic force to produce a maximum value of K_m , Kenytite develops an early maximum. A sample was tested as a powder against the phosphor-bronze strip and gave the following figures:—

H	26·5	48·5	72·2	103	134
K_m	253	291	318	302	300×10^{-6}

In the present experiments a sample weighing 3·08 grm. in powder form was tested at values of H ranging from 19 to 326, and the results confirm the earlier figures. The composition of this dark volcanic-looking rock is of course known, but it is interesting to note that it contains small detached portions of magnetite. Its absolute density is 2·573.

Franklinite.—The mass-susceptibility of a piece of this mineral weighing 2·69 grm. when tested in a portable instrument† was 0·00064, the value of the magnetic force, H, being 160. The present tests are in good agreement and indicate a maximum value when the force is equal to about 248 C.G.S. units.

Green Serpentine (2·50 grm.).—This rock was tested in the form of powder against the torsion of the phosphor-bronze strip and gave the following values of the susceptibility:—

H	69	95	155
K_m	135	139	169×10^{-6}

The agreement with the present experiments is satisfactory. The magnetic force, H, ranged from 19 to 270 C.G.S. units. As in the case of Franklinite the maximum susceptibility occurs at large values of the force, H.

Grey Granite.—A piece of this normal granite from Mount Sorrel, Leicestershire, has already been reported upon.‡ Its mass-susceptibility for $H = 41$ was 764×10^{-6} . When tested in the present instrument the mass-susceptibility varied from 510 to 599×10^{-6} as the force, H, was varied from 22 to 153 C.G.S. units.

* 'Proc. Phys. Soc.,' vol. 31, Part V (1919).

† 'Proc. Phys. Soc.,' vol. 31, Part V, p. 338 (1919).

‡ 'Phil. Trans.,' A, vol. 219 (Appendix), pp. 83–87 (1919). Also 'Roy. Soc. Proc.,' A, vol. 96, p. 429 (1920).

Copper Ferrite (2.54 gm.).—When tested over a range of H of 6.4 to 42.2, the mass-susceptibility varied from 0.0102 to 0.0169.

Ferrous Oxide (0.70 gm.).—The susceptibility (K_m) of this specimen varied from 0.0128 to 0.0211 as the force, H , was varied from 6.4 to 82.4.

In conclusion, I wish to thank Prof. E. F. Herroun for help received in the making of the instrument.

Double Refraction and Crystalline Structure of Silica Glass.

By LORD RAYLEIGH, F.R.S., Professor of Physics, Imperial College,
South Kensington.

(Received December 4, 1920.)

[PLATES 7-9.]

§ 1. *Introduction.*

Silica glass, as is well known, may be produced by the fusion of clear crystalline quartz. In this way a clear transparent product is obtained. The present paper deals only with this kind of silica glass. The cruder variety, known as vitreosil, which is prepared from sand, is not free enough from bubbles and striæ to allow of satisfactory observation.

That silica glass may be doubly refracting was noticed in casual observations, made to test its suitability for windows, in my experiments on the scattering of light by gases. It soon became clear that this double refraction could not in all cases be due to stress, but was to be attributed to something of the nature of crystalline structure. At the same time, the double refraction is very weak indeed compared with that of crystalline quartz.

Glasses have generally been considered essentially amorphous, and, indeed, this property would usually be invoked in the definition of a glass. It may be that, in view of the present results, the definition will need to be modified, though this point is hardly ripe for discussion. In the meantime, I still use the term silica glass.

I have not met with similar effects in any of the ordinary complex glasses. When these are doubly refracting, it is always attributable to strain.

§ 2. *Method of Observation.*

Since weak double refractions are to be examined, it is necessary to have a really dark field, when looking or photographing through the crossed nicols.

Lenses or protective glass covers between the nicols should be dispensed with, and, when glass must be used, as, for instance, if the specimen is immersed in a tank of liquid, the glass should be thin and free from stress.

Light from a "Pointolite" lamp was made slightly convergent by a condenser. It was polarised by a large nicol. After this it traversed the specimen. After an interval of a few inches came the analyser, a square-ended nicol of about 1 inch square aperture. Immediately following was a photographic lens of 5 inches focal length, arranged to give a two-fold magnification on the ground glass or photographic plate. On removing the ground glass, the image could be examined with an eyepiece if desired.

Larger magnification is often desirable. In my experiments it was got by enlarging the negatives. It would have saved trouble, however, to photograph on a larger scale. This was sometimes done with a 1-inch (single lens) microscope objective. The working distance of such an objective will, however, only admit a short analyser, and therefore one of small linear aperture. Hence only a small area on the specimen can be included. The ordinary lens and analyser would have been better with a camera several feet in length.

An ordinary polarising microscope, as used in petrology, is of no use for this work. But if a small square-ended analyser is mounted below the objective instead of above it, as usual, small specimens can be examined satisfactorily. A single lens achromatic objective of 1-inch focus was used. Higher powers are scarcely applicable.

Cut and polished slices of silica glass are, of course, the most satisfactory for observation. For quick examination polishing may be dispensed with, and the specimen examined in a trough of carbon tetrachloride, which has almost exactly the same index as fused silica. This, moreover, allows the specimen to be turned about and examined in any direction. The glass troughs used were cemented with seccotine. Specimens may also be mounted in glycerin, with thin micro cover-glasses.

§ 3. *Fused Silica in the Mass.*

Plate 7, fig. 1, shows a disc of fused silica, 2.5 mm. thick, and magnified 2 diameters. It will be observed that the field of view is covered with a granular pattern, the actual dimensions of the grains being about 0.5 mm.; further, the field shows large bright and dark regions covering many grains, and each occupying a good fraction of the whole picture. These latter regions are due to stress, and their positions can be shifted, temporarily by screw pressure applied to the edges of the plate, or permanently by heating to a yellow heat in the upper part of an oxygen blowpipe flame.

The mosaic pattern, on the other hand, is attributed to a crystalline or quasi-crystalline structure. The full evidence for this view will appear in the sequel. In the meanwhile, it is convenient to assume the truth of it.

It would be expected that a stress over a whole region, if of suitable amount, would tend to make the pattern more conspicuous. As an illustration of this, let the planes of vibration of the (crossed) nicols be at 45° to the vertical. Imagine three similar grains, a , b , c , each producing a relative retardation, which is only a very small fraction of a wave, as in the actual case. Let the maximum elasticity of a be vertical, of b at 45° , of c horizontal.

Then the intensities will be

$$a \ 1 \text{ (assumed),} \quad b \ 0, \quad c \ 1.$$

Now suppose a shearing stress applied to all three grains of such intensity and direction as to compensate the double refraction of a . Then the intensities will be

$$a \ 0, \quad b \ 1, \quad c \ 4.$$

So that the whole range of intensities is increased four times. This is the most favourable case. A much larger stress will flood the field with light, and obliterate the contrast due to the grains.

In agreement with these considerations, it can be observed in the photograph (Plate 7, fig. 1) that the grains are seen most clearly in regions intermediate between the brightest and the darkest regions of the picture.

One silica disc, 3 inches in diameter, showed a symmetrical distribution of stress, in the form of a dark cross, marking the planes of the nicols. This corresponds with what is often seen in glass discs. The structure was too large to be all covered at once by the polarising nicol, thus, I am unable to reproduce it in a photograph.

The photograph (Plate 7, fig. 1) is taken from a disc 2.5 mm. thick. This thickness will, as a rule, contain several grains, and overlapping causes complication. A slice of only 0.39 mm. thick, which would not allow of much overlapping, was mounted in the polariscope with thin cross-wires stretched over it, to serve as axes of reference. Photographs were taken with the (crossed) nicols in several successive positions, differing by $22\frac{1}{2}^\circ$, keeping the specimen fixed. On comparing these photographs carefully, it appeared that there was no part of the field which did not brighten up at some stage. The area seems in this particular case to be entirely occupied by the doubly refracting grains without any isotropic background.

It is possible that these grains correspond with the fragments of crystalline quartz, oriented at random, from which the silica glass was made, though of course their structure can only be a rudimentary vestige of the original

structure, which has a double refraction of quite a different order of magnitude. The size is not inconsistent with this view. If this were the case, we should expect that the structure would not be completely reconstituted after melting and solidifying (if these terms may be applied to a substance without a definite melting-point). Experiment shows that in fact the structure does survive melting to a considerable extent. It is difficult to make any satisfactory examination while it is white hot, because the field of view is flooded with false light; but a small piece of silica glass sheet was photographed and then heated to the highest temperature of the flame, avoiding mechanical deformation while soft as far as possible. On cooling, it was photographed again.

To compare the photographs, the latter one was reversed in the enlargement. The two were then trimmed along a corresponding straight line and mounted edge to edge. A considerable measure of symmetry was found between them, showing that much of the structure had survived (Plate 7, fig. 2). I am inclined to think from other experiments that even the parts which have apparently changed may still contain the old structure in a latent form, and that it might reappear under suitable conditions.

One of the most interesting properties of the doubly refracting grains is that they are capable of flowing into elongated shapes, like the liquid crystals of Lehmann. To show this, a strip was cut with the glazier's diamond from a plate showing the granules, and it was heated and drawn out in the oxy-gas blowpipe. It was immersed in a tank of carbon tetrachloride with its length bisecting the angle between the crossed nicols. The result is seen in Plate 7, fig. 3.

§ 4. *Elongated Fibres seen in drawn Silica Rod and Tube.*

For further study of these elongated crystalline fibres, it is convenient to make use of the drawn rod obtainable commercially. Sections of this, cut parallel to the length (plankwise) show the fibres admirably. They may also readily be observed in the round rod, using a carbon tetrachloride tank.

The fibres are most distinct at 45° to the planes of the nicols (Plate 7, fig. 4). They disappear when parallel to one of these planes (Plate 7, fig. 5); in other words, the fibres give straight extinction. The background not occupied by fibres remains dark in either position; thus it is devoid of double refraction. If we suppose that the material was originally like the granular specimen above examined, it would seem that in the process of heating and drawing, part of the material must have become isotropic, the crystalline portion shrinking somewhat. I have, in fact, observed an apparent contraction of the grains when a specimen was kept for some minutes at about 1000°C .

Returning to the longitudinal fibres seen in fig. 4, their breadth is in general about $1/200$ of an inch (0.13 mm.). I am not here speaking of the heavy double strip up the middle which will be discussed presently. The breadth was determined from a thinner slice of the same, where there is little overlapping of the fibres. Much thinner rods have been examined, down to 0.4 mm. diameter. The fibres can still be made out in carbon tetrachloride, using the microscope with a small nicol in front of the objective. In this case they are, of course, extremely narrow.

Griffith* has shown that thin drawn quartz rods have an extraordinary and abnormal strength immediately after drawing. He has shown that after touching solid objects they lose this abnormal strength. At Dr. Travers's suggestion, I examined a drawn rod in this condition to see if it showed the usual crystalline fibre. I found that it did. After the observation the rod was severely bent, and the curve which it took was marked down on paper. It was then stroked with another silica rod and bent again, when it broke long before reaching the curvature which it had endured before.

The experiment appears to leave little hope of connecting the appearance in the polariscope with the abnormal strength. But, conceivably, careful photographs taken before and after stroking might reveal something.

A transverse section of rod shows the same fibres cut across. It is remarkable that these fibres should show up in the polariscope. If the fibres behaved like uniaxial crystals with the optic axis along the length, there would, of course, be no double refraction observable in a transverse section. In addition to the irregularly distributed fibres which occupy most of the cross-section, there is a remarkable regular structure stretching diametrically across the section (see Plate 8, fig. 6), suggestive of a caterpillar, and conveniently so referred to. Along the middle of this line the section is penetrated by a series of tubular streaks, which are readily visible in the original uncut cylinder as lines, all lying approximately in a diametral plane and visible in the section with a magnifier as tiny dots.

The caterpillar structure gives straight extinction on this middle line (see Plate 8, fig. 7).

A longitudinal section may be oriented so as to cut across the caterpillar, in which case the caterpillar is seen as a central stripe (see Plate 7, fig. 5), or it may be cut so as to include the length of the caterpillar in its plane. In this case the field is filled with bold stripes (Plate 7, fig. 8). In both cases the extinction is straight, but in the second case no definite relation to the caterpillar structure is apparent without the help of a mica plate, as will be described presently.

* 'Phil. Trans.,' A, vol. 221, p. 163 (1920).

It appears that in the caterpillar we see in cross-section a series of crystalline fibres or ribbons all having their length along the rod, their breadth perpendicular to the length of the caterpillar, and their thickness along the length of the caterpillar.

Regarding each such ribbon as a rectangular solid, the optical observations described are summarised by saying that it gives straight extinction on every face. Advantage has been taken of this special structure to estimate the strength of the double refraction. Looking along the length of the caterpillar, *i.e.*, through the thickness of the ribbons, we have a series of crystals all arrayed in the same way, and pretty closely packed together, though apparently there is isotropic material between them. These crystals all cooperate, and by using a thick slice a relative retardation can be got large enough to be easily measured. The (longitudinal) slice used was 7.1 mm. in thickness, and showed a stripe as in Plate 7, fig. 4.

For estimating the double refraction, a quartz wedge was used with the axis of the crystal along its length.

The specimen was superposed on it, length to length, so that, between crossed nicols, the stripe crossed the coloured bands showing Newton's scale of colours. The place where it crossed the narrow and well-defined band corresponding to the tint of passage, was marked by a displacement of the latter towards the thick end by 2.5 mm. as measured on the ground glass screen of the camera. The distance between two successive order on the same (magnified) scale was 12 mm. Thus the relative retardation in the stripe was 0.21 of a wave, or, per millimetre thickness 0.029 of a wave. Crystalline quartz, perpendicular to the axis, would give an effect no less than sixty times as great.

A similar determination was made on a transverse section of the rod, 12 mm. thick. The caterpillar was placed along the length of the quartz wedge, and displaced the sensitive tint to the thick end of the wedge by 3.5 mm., on the same scale as before. Thus 1 mm. thickness would give 0.029 wave retardation, for light travelling along the rod. This is about the same as the value in the previous case; indeed, the measurement is not good enough to decide which is the larger.

In the third direction a considerable thickness cannot be got, but it was established that the double refraction in this direction was such as to cooperate with a quartz wedge with its length parallel to the fibres, instead of neutralising it. The quartz wedge is here introduced only for convenience of statement. The actual determination was made by means of a plate of mica, giving the sensitive tint. A silica rod was rotated about its (vertical) axis in the tank. When the structure was edge on, a yellow stripe was seen,

of lower tint than the mica alone. When it was broadside on a broader blue band appeared of higher tint than the mica alone and of breadth equal to the length of the caterpillar, which showed that it belonged to that structure.

In this case then if we observe at right angles to the length of a fibre, the greatest optical elasticity is along the fibre in one azimuth, and perpendicular to it in the other.

I have however met with another specimen which behaved quite differently. In this case one particular fibre was so thick and conspicuous that it could be followed individually right through a rotation. The tint was blue or green, and therefore the fibre cooperated with the mica in all azimuths. It was suspected that the strength of the action varied in different azimuths, but this would be expected in any case if the fibre is not of circular cross-section.

Since all fibres are not alike, we may perhaps suppose that when a fibre originates in a grain, which of the principal directions will be stretched depends on the accident of how the grain is oriented.

With regard to the origin of the caterpillar structure, it appears to be intimately connected with the way in which the silica is worked. Some observations on the transverse section of silica tubes show that they are sometimes lined internally with ribbon-like crystals, the breadth of the ribbon lying along the radius. If a tube of this kind is flattened and collapsed, something like the caterpillar structure may be expected, and it survives the drawing-out process. The minute holes along the central line of the caterpillar represent imperfect closing up when the original cylinder is collapsed.

The actual dimensions of the ribbons are not of special significance, depending as they do on to what length the mass of viscous silica is drawn out. Those in the specimens photographed were often about $\frac{1}{2}$ mm. broad and $1/10$ mm. thick. The caterpillar was 6 mm. long, and 1 mm. broad, and the median line, which was best seen in a longitudinal section (fig. 4), separated the crystalline ribbons by about $1/10$ mm.

The fact that these longitudinal fibres or ribbons allow of being drawn out to large multiples of their original length seems to assimilate them to Lehmann's liquid crystals. To study their behaviour further, a rod 1 cm. diameter was drawn down locally in the blowpipe, so as to give it a waist of about half this diameter, carefully avoiding any twist while the material was soft. The material was then ground down to form a plank in section about 2 mm. thick, which included all the conspicuous fibres of the caterpillar structure. A photograph, with nicols set at 45° to the length, is shown in Plate 8, fig. 9. It will be noticed how the fibres bend in at the waist.

By rotating the crossed nicols relative to the section, it was established

that, when they are inclined to the original direction (greatest angle about 20°), the position for extinction is along the direction of the fibre *at the point examined*. In other words, for extinction, the nicols must be along the tangent and normal to the (curved) fibre. The direction of extinction follows the sinuosities of the fibre itself.

The same was observed in a thinner rod, bent twice at right angles, and immersed in carbon tetrachloride, to annul refraction.

Returning to the case of a drawn-out rod, it was interesting to examine the effect of twisting it while soft. Plate 8, fig. 10, shows this. A twist of 180 degrees was given, and the section prepared as before. The confusion of the fibres which results is very apparent.

The fibres evidently persist very obstinately when the material is heated and drawn. I have not succeeded in getting rid of them in a rod, even when it was kept fused for some minutes at the highest temperature of the flame, though in this way all visible streakiness was got rid of, and the rod was shortened and thickened.

Plate 8, fig. 11, which is a silica crucible lid, shows this persistency of the fibres. Incidentally, it suggests how the lid has been made from the bottom of a bulb blown from tubing.

§ 5. *Bright Crosses.*

Silica glass sometimes shows bright crosses in polarised light, which are very brilliant compared with the crystalline structure which has been discussed (fig. 11). These crosses are found, so far as my experience goes, only in silica which has not been repeatedly reheated and worked. They are commonest in material that has only been heated once, and are never found in drawn rod and tube, or in built up optical silica.

Examination with an ordinary polarising microscope shows that they are always centred on an inclusion in the silica glass, which itself shows relatively strong double refraction, and which may have dimensions comparable with 0.1 mm. or 0.2 mm. The cross itself is much larger, say 1 mm. or 2 mm., and is situated in the silica glass, the inclusion merely occupying the centre.

These crosses are obviously due to stress, and may be closely imitated by driving a conical metal plug into a piece of sheet celluloid (Plate 8, fig. 12).

At first the two cases were considered identical, the stress being referred to differential contraction during cooling. It occurred to me, however, that the inclusion would almost certainly shrink very much more than the glass, which has a quite exceptionally small expansion coefficient. In this case the only possible system of stresses would be a radial tension and a

circumferential compression, whereas in the plugged celluloid these relations are inverted.

The two structures were arranged side by side in the field of view, and a plate of mica giving the sensitive tint (one wave retardation for the yellow) was superposed. It was found that, if, *e.g.*, the first and third bright quadrants in the silica cross raised the interferential tint, the same quadrants in the celluloid lowered it. The fact that there is a radial tension round the inclusion shows that the surrounding glass does not part company with it on shrinking.

The inclusions were kindly examined by my colleagues, Prof. Watts and Mr. A. Holmes, using petrological methods. They came to the conclusion that these consisted of crystalline quartz, and this is in harmony with the fact that it is the less worked samples of silica glass which contain them. Still, it seems somewhat mysterious that they should remain unmelted and retain their sharp outlines after even one melting of the entire surroundings.

§ 6. *Optical Silica.*

This is built up by the slow addition of powdered material to a mass slowly rotated and traversed.* In this way a cylindrical mass is obtained, which may be cut into circular discs. Such discs examined between crossed nicols show a remarkable structure (Plate 9, figs. 14, 15) in which the spiral course in which the material is built up is traceable, particularly near the middle.

The photographs show a resemblance to the interference figure of a uniaxial crystal in convergent light, but this resemblance is merely superficial. The successive black rings in figs. 13, 14 do not represent successive orders, but each is a return to zero retardation. No colours are seen, the retardation being in no case more than a fraction of a wave. Moreover, the rays used are *not* appreciably convergent, but all nearly perpendicular to the plate itself.

The appearances are, I believe, due in the main to stress, but the granular crystalline structure is seen superposed on it: the latter is best seen in the less bright parts of the pattern; but is traceable over the greater part of fig. 13.

Most of the structures already considered are *not* attributed to stress, and the question presents itself, what definite criterion have we for deciding between stress and crystalline structure?

The answer is that double refraction of an element of volume due to stress necessarily depends on the forces exercised upon it by the neighbouring parts; and if these forces are changed by cutting the material away, the double refraction will be changed in strength and direction—though not necessarily made weaker.

* Kent and Lacell, British Patent No. 10930 of 1910.

On the other hand, a purely crystalline pattern will be unaffected by cutting neighbouring material away.

To apply this criterion to the case of the "optical" silica, a circular disc was cut into sectors, and two of these were reassembled by cementing them in their original relative positions with canada balsam on a piece of glass.

The preparation was placed between crossed nicols, with their principal planes at 45° to the line of section, thus bringing the rings, where interrupted by the cut, into the most favourable position for brightness. A photograph was taken (Plate 9, fig. 16) which shows that each bright ring is interrupted at some little distance on either side of the cut, the interruption being comparable with the breadth of the ring. In this case the effects *are* due to stress and the stress is of such a kind that the material can relieve itself near the free edge, and shows no double refraction there.*

The two brightest rings are in circumferential compression and radial tension, but the intermediate ring, which is broader and less bright, is in the opposite state. The conditions of equilibrium require this, and the fact was verified by superposing a mica plate showing the sensitive tint. If this was so turned as to lower the interferential tint of the outer and narrower rings, the tint of the intermediate bright ring was raised. The sign of the stress was determined by comparison with celluloid stressed by a metal plug forced into it.

It was also determined by the application of radial pressure in a screw press. This had the effect of darkening the two narrower bright rings, and brightening up the intermediate broader one. If the pressure was adjusted so as to quench the bright rings, then the granular crystalline structure came into view. This and other observations show that it is merely masked by the bright rings, and is present all over the outer parts, at least, of the specimen. As regards the inner parts of these discs it is more difficult to speak. Plate 9, fig. 14, seems to show the granular structure all over, but Plate 9, fig. 15, is more suggestive at first sight of fibres wound up into spiral form in the regions near the centre. Upon the whole, however, I believe that the central part of fig. 14 represents a stress structure.

At all events, the facts above mentioned seem to decide in favour of stress as an explanation of the conspicuous outer rings. We may contrast this case with that of the longitudinal stripes seen in a plankwise section of a drawn rod (figs. 4, 8). These stripes in many cases extend to the very edge, though, of course, there are some that fade out in that neighbourhood as in any other part of the specimen. Special note may be taken of the

* Another kind of stress effect is seen in Plate 7, fig. 5, where the position of the nicols is such as to show nothing of the true crystalline fibres.

broad double stripe in the middle, which is a section of the caterpillar structure.

Returning to Plate 9, fig. 15, it is suggested to me by Mr. Reynolds, of the Silica Syndicate, that the bold outer rings are probably connected with a periodic general reheating of the mass in the electric arc furnace, which is found necessary in the course of laying on the outer layers of material. But I confess it is not clear to me how this should produce stresses. One would rather expect it to alleviate them, as it is intended to do.

Some tests were made of the effect of a steady temperature, estimated at about 1000°C ., on the optical silica discs.

I give these experiments in detail, stating all that was done, though it may be that some points are unessential.

A silica disc, as received, was cut into two thinner discs, each about 1 mm. thick, and the sides polished by the optician. After one of them had been photographed in the polariscope, both discs were placed in a platinum crucible, heated in a Meker furnace, and kept at a full red heat for about two hours. After that time they were taken out, and, in order to examine them at once, they were quenched in water. It was anticipated, from the usual behaviour of articles made of silica, that this could be done without harm. In fact, however, the (polished) surface showed a superficial network of fine cracks.* These were ground out and the surfaces repolished. A photograph taken after that showed that the structure had entirely disappeared (Plate 9, fig. 17).

One of the discs was further heated under the same conditions for about ten minutes, and observed and photographed again. To my great astonishment the structure had to a large extent reappeared (Plate 9, fig. 17), and it showed not only the crystalline granules, but also the ring structure, which (on the evidence above given) is attributed to stress.

Although I saw no possibility of mistake, yet it was satisfactory to be able to repeat the test on the other specimen with the great advantage of knowing what to expect. In this case the structure, quite invisible at first, came out distinctly in five minutes. It attained the fullest re-development in about twenty minutes and then gradually faded again, and in an hour from the start had almost gone. These times were noted from the commencement of the reheating, but include only the time actually in the furnace, and not the time needed for examination. Photographs were taken at each stage.

I do not know what is to be thought of these effects. No doubt much further work is needed to elucidate them, but I have not thought it well

* This may have been due to some modification of the surface produced by the polishing operation.

either to delay further the appearance of this paper or to omit all mention of them. With further prolonged heating, devitrification occurs in all kinds of silica glass. This is generally regarded as due to the formation of tridymite, which is of much stronger double refraction than the structure here discussed. Upon the phenomenon of devitrification I do not enter.

§7. Summary.

1. Although glasses in general have no double refraction, except that due to bad annealing, yet silica glass is found to have a doubly refracting structure, which cannot be so accounted for, and must rather be regarded as crystalline.

2. The double refraction is very weak, of the order of one-sixtieth that of crystalline quartz.

3. In a mass of silica which has been melted, but not drawn or blown, the structure consists of doubly refracting grains, with dimensions of about $\frac{1}{2}$ mm., oriented at random. These grains may correspond to the original fragments of quartz, which were melted to form the glass, but this is uncertain. At all events, the grains are very persistent and individually survive a remelting of the material.

4. If the grained material is drawn out while soft, the grains are elongated into crystalline fibres or ribbons. These fibres always give "straight extinction" in the polariscope, and their length is along one axis of the *elipsoid of optical elasticity*, but apparently not always along the same axis. The fact that the crystalline grains can be made to flow in this way assimilates them to Lehmann's *liquid crystals*.

5. If the material is bent or twisted the fibres follow its course unbroken, and are always extinguished in the polariscope if the nicols are set along the tangent and normal to their direction at any point.

6. Fused silica sometimes contains isolated small inclusions of quartz, with angular outlines, which have escaped vitrification. These are conspicuous in the polariscope by the strain effects they produce in the surrounding glass.

7. Discs of "optical silica," which are built up by a special process, show a most curious strain structure, on which the crystalline grains are superposed.

A heat treatment is described which resulted in the complete disappearance of all this structure and its subsequent reappearance.

In conclusion, I wish to express my best thanks to Lady Rücker for the loan of large nicol prisms, which have greatly facilitated the work.

DESCRIPTION OF PLATES.

PLATE 7.

- Fig. 1.—Disc of silica, ordinary quality. $\times 2$ diameters.
 Fig. 2.—Sheet silica, ordinary quality. As received right half. After fusion left half. $\times 4$ diameters.
 Fig. 3.—Strip of sheet silica. Ordinary quality. Lower part drawn out in oxygen blowpipe. $\times 2$ diameters.
 Fig. 4.—Plankwise section of silica rod. Nicols at 45° to the length. $\times 2$ diameters.
 Fig. 5.—The same. Nicols parallel and perpendicular to length. $\times 2$ diameters.
 Fig. 8.—Plankwise. Section at right angles to the previous (figs. 4 and 5). Nicols at 45° . $\times 2$ diameters.

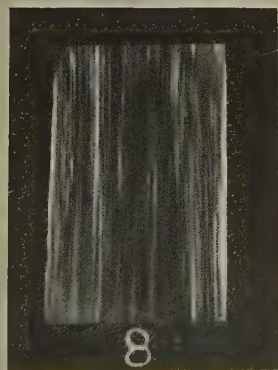
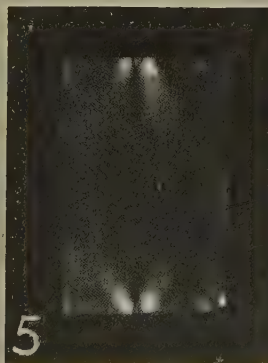
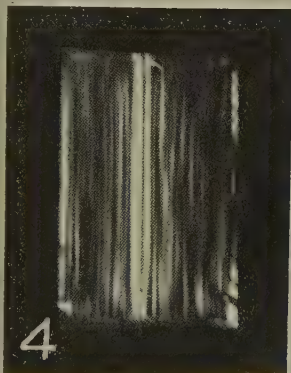
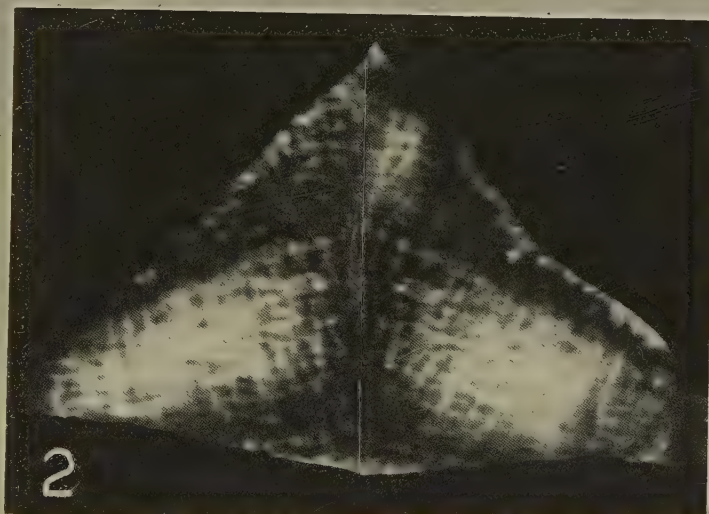
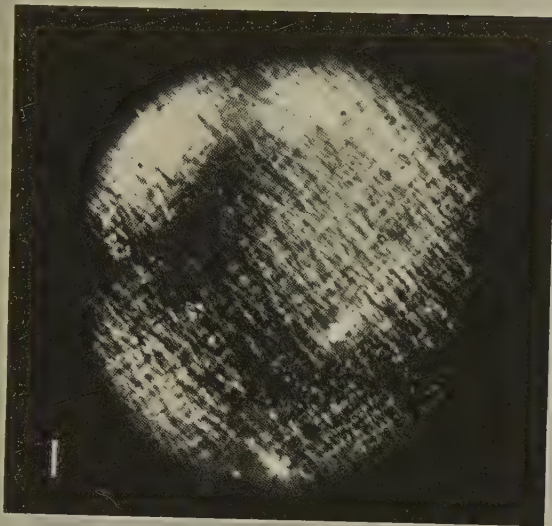
PLATE 8.

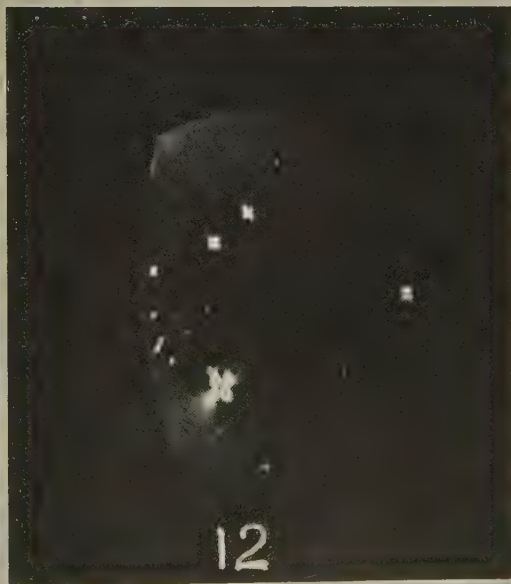
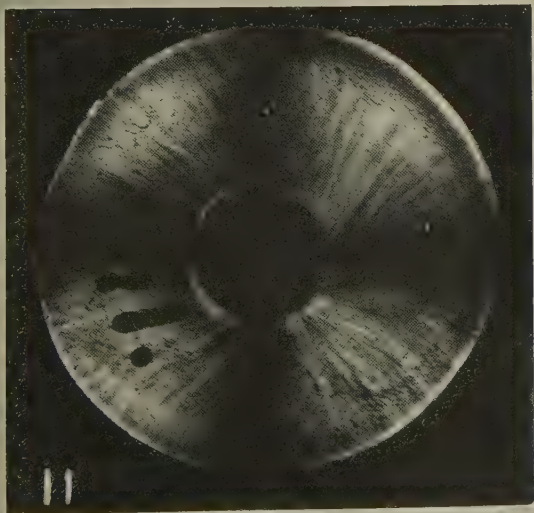
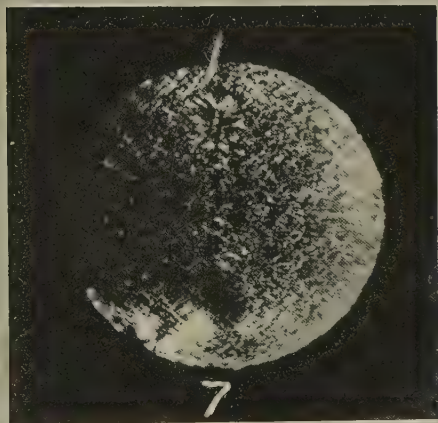
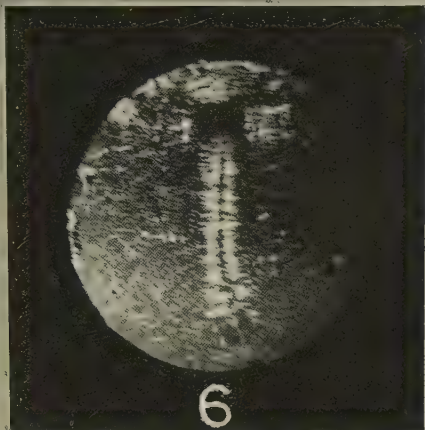
- Fig. 6.—Transverse section of a drawn silica rod. Nicols at 45° . $\times 4$ diameters.
 Fig. 7.—The same. Nicols at 45° . $\times 4$ diameters.
 Fig. 9.—Section similar to fig. 8 (Plate 1), but rod drawn out in blowpipe before cutting section. $\times 2$ diameters.
 Fig. 10.—Similar to fig. 9, but twisted through 180° in the process of drawing out. $\times 2$ diameters.
 Fig. 11.—Lid of silica crucible. $\times 2$ diameters.
 Fig. 12.—Plate of ordinary quality silica. Shows bright crosses each entered on an inclusion of crystalline quartz. $\times 2$ diameters.

PLATE 9.

- Fig. 13.—Sheet celluloid, stressed with metal plug, in imitation of No. 12. $\times 2$ diameters.
 Fig. 14.—Disc of optical silica, as received. $\times 2$ diameters.
 Fig. 15.—Another ditto. $\times 2$ diameters.
 Fig. 16.—Sectors of a silica disc, cut and reassembled. (Part of each sector only is shown.) $\times 6$ diameters.
 Fig. 17.—Disc No. 15, after heating to redness for two hours and quenching. $\times 2$ diameters.
 Fig. 18.—The same, after further heating. $\times 2$ diameters.

Note.—The photographs 15, 17, 18, though they represent the same disc, are not on exactly the same scale, nor similarly oriented. The nicol used as analyser in all cases slightly distorts the circular outline, making it oval.





The Magnetic Mechanical Analysis of Manganese Steel.

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One of the most interesting alloys for the study of its magnetic properties is manganese steel. The following paper is an attempt to correlate some of the magnetic and mechanical properties of manganese steel, in the hope that as such data are circulated it will eventually be possible to interpret from the magnetic behaviour of steel what the mechanical properties will be.

Six manganese steel rods supplied by one of the authors were drawn from the same source, 76 cm. long and 0.95 cm. in diameter, and used "as drawn." These rods were marked 1, 2, 3, 4, 5, and 6 respectively. The chemical analysis was made on rod No. 4 and showed:—

C	1.25 per cent.
Si	0.43 "
Mn	12.20 "

The record for the heat treatment was as follows:—"All six bars were treated at 1000° C. (five minutes), and then water-quenched in ordinary cold water. Nos. 1, 5 and 6 were then enclosed in an iron pipe welded over at the ends, and annealed. The time for cooling from 550° C. to 450° C. was about eight hours. As this treatment did not make the bars sufficiently magnetic they were again annealed at 500° C. (530° C.—475° C.) for sixty hours."

Rough tests were made on the rods (without removing outer skin) with balanced hand magnet. Rods Nos. 2, 3 and 4, were non-magnetic; hand magnet just pulled at 1/16 inch. Rods 1, 5 and 6 were magnetic; hand magnet pulled well at 3/8 inch. About 25 per cent. Sp. Mag. (S.C.I.—Swedish Charcoal Iron = 100). From these six rods Nos. 2 and 5 were selected to represent the non-magnetic and magnetic types respectively, one differing from the other only in heat treatment.

These rods were used to study the changes in length which occur when a ferro-magnetic substance is subjected to a magnetic field, as well as the effects upon the values of the intensity of magnetisation when the rods are subjected to a longitudinal stress. It would appear, therefore, that more and more is it going to be possible* to determine what will be the mechanical properties of

* Burrows, 'Sci. Paper, No. 272, Bur. Stands.'; Williams, 'Jour. Cleveland Eng. Soc.,' January, 1917; 'Topical Discussion on Magnetic Analysis, A.S.T.M.,' June Meeting, 1919; Gebert, 'Jour. A.S.T.S.,' June, 1919; Sanford and Kouwenhoven, 'Sci. Paper, No. 343, Bur. Stands.'

ferro-magnetic substances by a study of their magnetic behaviour. In the two relations which are to be studied in this paper we have an excellent avenue of approach to this fascinating subject.

The method* devised by one of us for determining the Joule effect (length changes), was employed in this work. The length of rods between brass extensions was 74.3 cm. In fig. 1 is shown the variations in length of rod, No. 5, as the magnetic field was increased from zero up to nearly 3000 Gauss. This shows that for all field strengths used, the change in length was an increment. In a similar way rod No. 2 was tried out but no changes in length could be detected, although changes as small as 0.000004 cm. could be read from the scale.

Working in the same vertical solenoid as used in the Joule effect, the rods were next tested for the effect of tension on the intensity of magnetisation (Villari effect). In the usual ballistic method for the measurement of the intensity of magnetisation of rods a small coil of wire is wound about the middle section of the specimen and the terminals of this exploring coil attached to a ballistic galvanometer. The rod thus equipped is placed in a long solenoid, to ensure as nearly as possible a uniform magnetic field. The throw of the galvanometer is then observed when the current is broken and reversed in the large solenoid. When this is done the charge flowing through the galvanometer is

$$Q = 2 \frac{\pi r_1^2 H n_1 + 4\pi I (\pi r_3^2) n_1}{R}, \quad (1)$$

where r_1 and n_1 are the radius and number of turns of wire respectively in the small exploring coil on the rod, r_3 the radius of the rod to be tested, R the resistance of the galvanometer and exploring coil circuit, H the field in the solenoid, and I the intensity of the magnetisation.

It will be seen from equation (1) that the deflection of the galvanometer depends on two main factors: the field of the solenoid and the flux induced in the rod. If the intensity factor happens to be small and H large, it will be hard to measure I with accuracy, as the deflection of the galvanometer due to it is only a very small fraction of the total reflection.

For the so-called non-magnetic rod No. 2 it was evident that there was some magnetic induction, otherwise the hand magnet would not have pulled at any distance, no matter how small; consequently, to measure the intensity of magnetisation in rod No. 2, especial care had to be used to emphasise the intensity of magnetisation factor in equation (1). This is accomplished in the following way: a second coil, having about twice the cross-section of

* Williams, 'Phys. Rev.,' vol. 32, p. 281, March, 1911; vol. 34, p. 258, April, 1912; 'Amer. Jour. Sci.,' vol. 36, p. 555, November, 1913.

the first exploring coil, but containing only about half as many turns, is placed over and concentric with the first exploring coil. The two coils are then connected in series with the ballistic galvanometer, so that, when the field, H , in the solenoid is varied, the E.M.F. generated in the first coil will just balance that in the second. When this is accomplished, we have the charge flowing through the galvanometer,

$$Q = 2 \frac{\pi r_1^2 n_1 H - \pi r_2^2 H n_2}{R} = 0, \quad (2)$$

where r_2 and n_2 are the radius and number of turns in the outer exploring coil. If, now, the manganese steel rod is thrust through all of the coils, the charge passing through the galvanometer, when the current is broken and reversed in the main solenoid, is

$$Q = 2 \frac{(\pi r_1^2 H n_1 + 4\pi I n_1 \pi r_3^2) - (\pi r_2^2 H n_2 + 4\pi I n_2 \pi r_3^2)}{R}, \quad (3)$$

whence from (2) and (3)

$$Q = \frac{8\pi^2 r_3^2 (n_1 - n_2) I}{R}, \quad (4)$$

i.e., since θ , the deflection of the galvanometer is proportional to Q , we can at once write,

$$\theta = kI. \quad (5)$$

If k can be determined, we have an absolute method* for the determination of I , which is workable when I is comparatively small. For the determination of k , the following method was employed: a long slender solenoid of radius r_4 , whose general dimensions were those of the rods tested, was made up and used in place of the rods. When the current in this slim solenoid was broken and reversed, a flux was produced in the two coils connected to the galvanometer and the charge,

$$Q = \frac{2\pi r_4^2 H (n_1 - n_2)}{R}. \quad (6)$$

Here $H = 4\pi n_3 i$, where n_3 is the number of turns per centimetre in the slim solenoid, and i the current flowing through it, hence (6) becomes

$$Q = \frac{8\pi^2 r_4^2 n_3 (n_1 - n_2) i}{R}. \quad (7)$$

If we exchange the rod for the coil, and *vice versa*, the deflections will be

$$\theta_1 : \theta = \frac{8\pi^2 r_3^2 (n_1 - n_2) I}{R} : \frac{8\pi^2 r_4^2 n_3 (n_1 - n_2) i}{R}, \quad (8)$$

* It is to be noted that this deduction holds only for infinitely long solenoids and rods. It is assumed in this work that the ratio of length to radius is sufficiently large to make any errors due to demagnetisation effects negligible.

whence solving for I we get

$$I = \frac{\theta_1 r_4^2 n_3 i}{r_2^3}. \quad (9)$$

In making the double coil which was connected to the galvanometer, wooden spools were used, the smaller one being just the size to fit into the larger one. The inner spool was wound with 1034 turns of No. 36 silk-covered wire, while the outer one had 520 turns of No. 28, the difference in size of wire making the coils about the same length. After carefully balancing the two coils against each other, they were fastened together firmly by boiling in beeswax and allowing the wax to harden between them. For the final adjustment, a coil of some twenty turns was wound on a spool which could be rotated so as to include more or less lines of force from the main solenoid. With this small coil in series with the double coil, an exact balance between the coils could be established. The balance was tested for field strengths up to 2000 Gauss, and no observable deflection of the galvanometer was present. In all of the circuits connecting these coils, it was very necessary to keep the wires leading to and away from the coils wound together, in order to avoid induction effects as much as possible.

In determining the effects of tension on the two manganese steel rods, coils of several hundred turns were wound directly on the rods. These coils were connected to a ballistic galvanometer, and the deflections observed when the current through the main solenoid was broken and immediately reversed, first without and then with a tension of 350 kgrm. on the rod. From the ratio of the two deflections and the values of I , as determined above, the per cent. and actual change in I were calculated.

Curve 1, fig. 2, shows the values of I for corresponding values of H in rod No. 5. These values are for the rod when not under tension. Curve 2, fig. 2, is a plot of the difference between intensity of magnetisation when under tension and when relieved of it. It will be seen that, for all field strengths, so far as we were able to go, the application of a tension increased the intensity of magnetisation. This is in harmony with the results shown in fig. 1, where the change in length was an increment for all fields. If a Villari reversal point had occurred, curve 2, fig. 2, would have crossed the axis for H , and the point of intersection would be the Villari critical point for the specimen of steel under investigation.

Rod No. 2 did not show any change in intensity of magnetisation by being stretched, just as it did not show any change in length in a magnetic field. Fig. 3 shows the value of I for rod No. 2. It will be noted that I is plotted to a scale thirty-five times as great as for rod No. 5 in fig. 2. A striking similarity between the two curves is shown when they are superimposed one

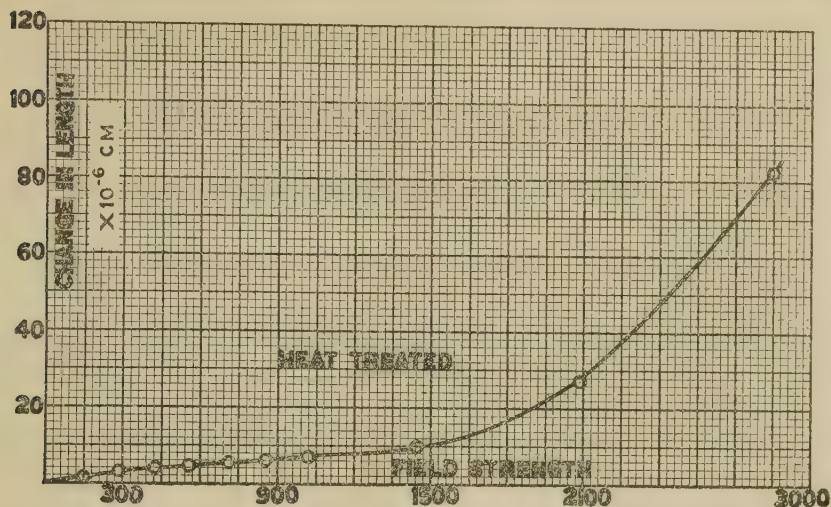


FIG. 1.

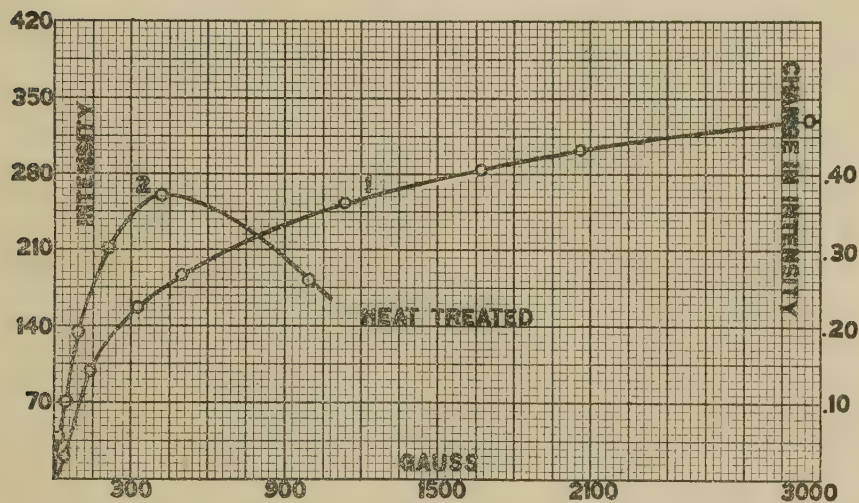


FIG. 2.

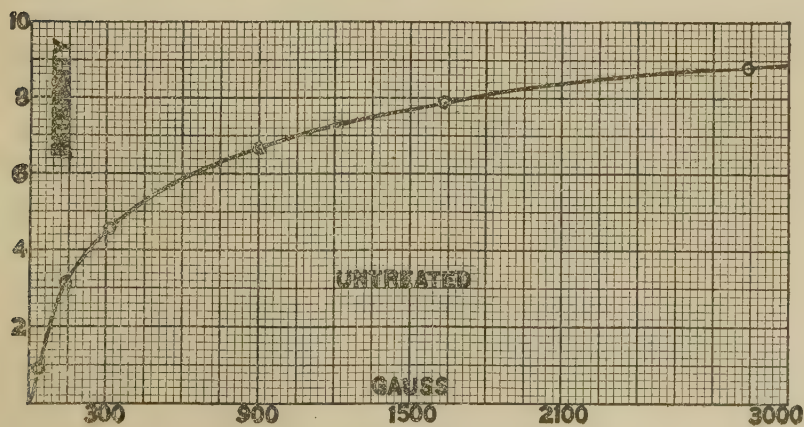


FIG. 3.

on the other. A factor of 36 instead of 35 would have made them almost exactly coincident.

It was thought probable this might be due to slight oxidation and alteration in composition of the surface of the bar, which can only be avoided in heat treatment by observing special precautions not taken in the present instance.

As pointed out, bars Nos. 2, 3, and 4 showed a very slight attraction with the hand magnet.

It was therefore decided to remove a few thousandths of an inch from the surface of bar No. 4 by means of emery cloth. The hand magnet was then applied to this bar, which did not show any magnetic susceptibility. The slight magnetic qualities noticed in bar No. 2 in fig. 3 were therefore entirely due to the condition of the surface material.

It should be added here that manganese steel is very readily oxidised, and consequently bars of it, unless carefully ground, are liable to what is termed "skin" trouble, that is, slight magnetic susceptibility. This arises from the temperatures employed in the heat treatment of this material, a very thin layer indeed being formed on the outer surface of the bar of oxidised material, which is slightly magnetic.

In the Joule phenomenon of magnetic lengthening, we have a very definite mechanical effect due to a magnetic field. In the Villari effect, we have, as the result of a mechanical pull, a very definite change in the magnetic properties of the steel. These are reciprocal relations, and furnish a method for magnetic-mechanical analysis. Whether we shall ever be able to interpret all of the mechanical properties of ferromagnetic substances from their magnetic behaviour is a question, but from what has been accomplished there are fair promises, and no avenue seems more inviting than the one which has been followed in this study, where the magnetic and mechanical effects are so closely associated. Here is a splendid opportunity for co-operation between the large steel industries with their resources of materials, and the research laboratories with their resources of skilled investigators, to make a very thorough study of this field. X-ray methods, and the methods indicated above, seem to be about all the means we have at present to test the mechanical properties of a substance without injuring the sample tested. There are some advantages in the magnetic method.

The Internal Energy of Inflammable Mixtures of Coal-gas and Air after Explosion.

By W. T. DAVID, M.A., D.Sc., Professor of Engineering, University College of South Wales and Monmouthshire.

(Communicated by Sir Dugald Clerk, F.R.S. Received October 28, 1920.)

The results of experiments upon the heat lost by radiation and by conduction during the explosion and subsequent cooling of inflammable gaseous mixtures have been recorded in previous papers.* In the first section of the present paper the experimental results for mixtures of coal-gas and air of various strengths have been combined, and an empirical law of cooling formulated.

In the second section of the paper the combined results have been applied to the estimation of the internal energy of the exploded mixtures at the maximum temperatures developed and at various stages during cooling. A study of the internal energy values for the different mixtures so obtained appears to throw into fair perspective the various causes responsible for the so-called "suppression of heat" in gaseous explosions—or, at any rate, in explosions of mixtures of coal-gas and air.

As is well known, the main theories which have been put forward to account for the low pressures developed are—

(i) Increase of specific heat of the products of combustion with temperature (MM. Mallard and Le Chatelier). Under this head may be included such dissociation as may occur, since it would naturally be included in all specific heat measurements;

(ii) Incomplete combustion (Sir Dugald Clerk); and

(iii) Heat loss to the walls of the containing vessel (Hirn).

The results given in this paper appear to show definitely that all these are important factors in limiting the maximum pressures developed;† and they enable a quantitative estimate to be made as to their relative importance in the various mixtures experimented upon.

Results of Experiments.

Full details of the experimental methods employed in the determination of the radiation and conduction losses will be found in the papers already

* 'Phil. Trans,' A, vol. 211, p. 375; 'Phil. Mag.,' January, 1920, p. 66, and 'Phil. Mag.,' September, 1920, p. 318.

† Sir Dugald Clerk, who put forward the theory of continued combustion in 1886, was not of opinion that it was the only cause limiting the pressure developed. He states very definitely that in his opinion the factors operating were complex. ('Proc. Inst. C. E.,' March, 1886.)

referred to. It will be convenient, however, to describe them here very briefly. The gaseous mixtures were contained in a cylindrical cast-iron vessel 30 cm. in diameter and 30 cm. in length, and were fired by means of an electric spark in the centre of the vessel. Continuous records of the pressure and of the heat loss during explosion and subsequent cooling were taken simultaneously. The radiation measurements are the mean of three sets of measurements made with the recording apparatus in three different positions on one of the end-covers of the explosion vessel; and it is believed that they give very approximately the mean value over the whole vessel. These values multiplied by the area of the interior surface of the vessel (4380 sq. cm.) should therefore give the total radiation loss fairly accurately. The conduction loss measurements are the average over a large portion of one of the end-covers. It cannot be stated with confidence that these measurements give an accurate indication of the mean value of the conduction loss over the entire surface of the vessel, but it is thought that they approximate sufficiently closely to this value to enable a fairly reliable estimate of the total conduction loss to be made.

The curves in figs. 1, 2, and 3 give the mean gas temperature and the

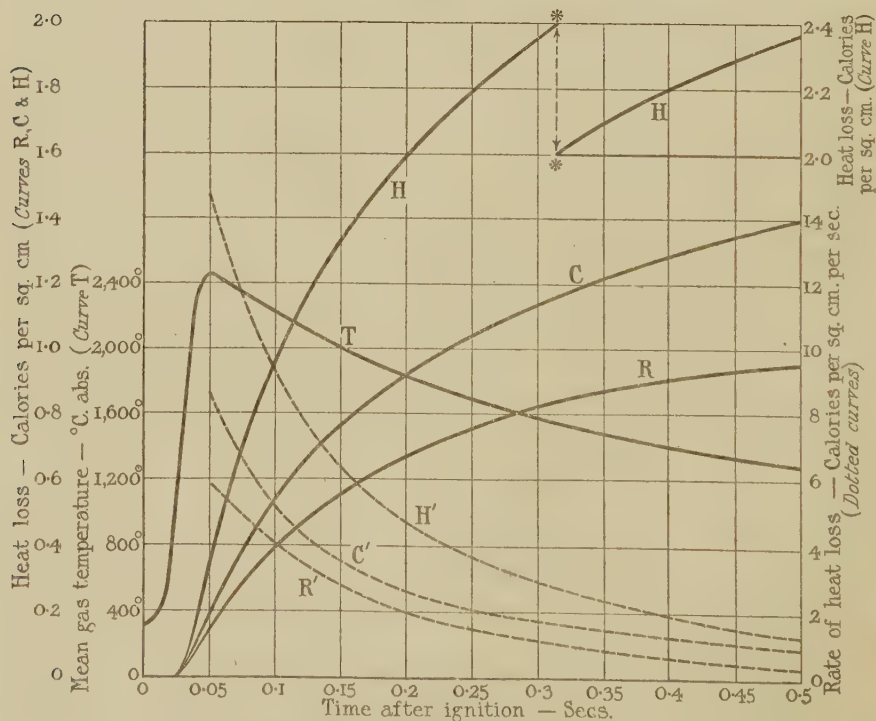


FIG. 1.—Heat-loss in 15 per cent. mixture coal-gas and air.

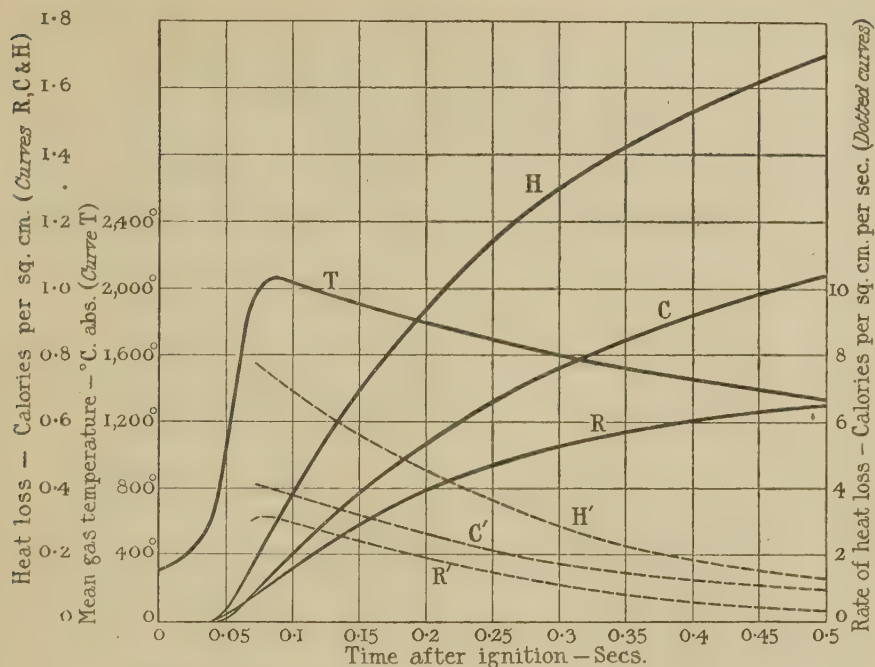


FIG. 2.—Heat-loss in 12.4 per cent. mixture coal-gas and air.

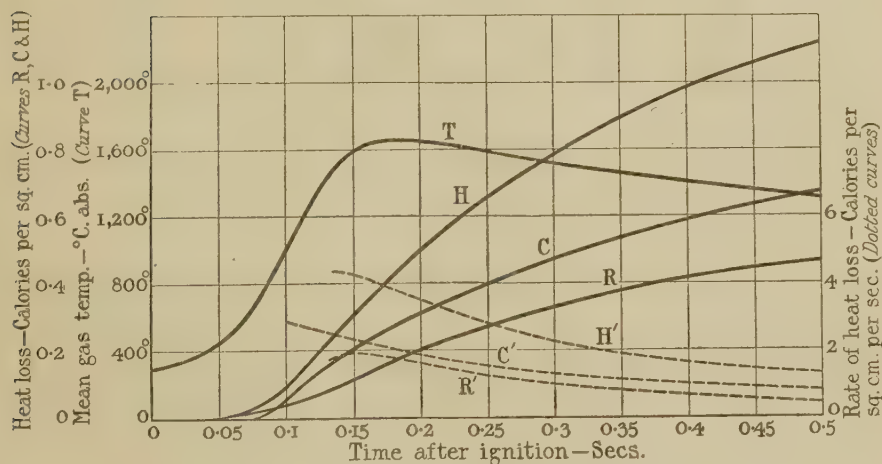


FIG. 3.—Heat-loss in 9.7 per cent. mixture coal-gas and air.

mean radiation and conduction losses per square centimetre of wall surface at various times after ignition in 15 per cent., 12.4 per cent., and 9.7 per cent. mixtures respectively. The T-curves give the mean gas temperature; the R-curves the mean radiation loss per square centimetre, the C-curves the mean conduction loss per square centimetre, and the H-curves the mean

total loss (*i.e.*, the radiation *plus* the conduction loss) per square centimetre. The dotted curves are the differentials of the heat loss curves (R, C, and H) and give the rate of heat loss (radiation, conduction and total) per square centimetre of wall surface per second. The data from which these curves have been drawn are given in Tables I, II, and III. The Tables also show the proportion of the heat of combustion of the coal-gas originally in the vessel which has been lost by radiation and conduction at various stages during cooling.

Table I.—Heat Loss in a 15 per cent. Mixture of Coal-Gas and Air. Heat of Combustion of Coal-Gas in Vessel = 16,300 calories.

Time after ignition (secs.).	Mean gas temperature (° C. abs.).	Heat loss per sq. cm. of surface.			Heat loss expressed as a percentage of the heat of combustion of the coal-gas.		
		Conduction.	Radiation.	Total.	Conduction.	Radiation.	Total.
0·05	2440 (max. temp.)	0·19	0·14	0·33	5·1	3·8	8·9
0·1	2220	0·54	0·39	0·93	14·4	10·4	24·8
0·15	2020	0·76	0·56	1·32	20·3	15·0	35·3
0·2	1840	0·92	0·67	1·59	24·5	17·9	42·4
0·25	1710	1·04	0·76	1·80	27·7	20·3	48·0
0·3	1600	1·13	0·83	1·96	30·0	22·2	52·2
0·4	1430	1·29	0·91	2·20	34·4	24·3	58·7
0·5	1300	1·41	0·96	2·37	37·6	25·6	63·2

Table II.—Heat Loss in a 12·4 per cent. Mixture of Coal-Gas and Air. Heat of Combustion of Coal-Gas in Vessel = 13,500 calories.

Time after ignition (secs.).	Mean gas temperature (° C. abs.).	Heat loss per sq. cm. of surface.			Heat loss expressed as a percentage of the heat of combustion of the coal-gas.		
		Conduction.	Radiation.	Total.	Conduction.	Radiation.	Total.
0·08	2050 (max. temp.)	0·17	0·14	0·31	5·5	4·5	10·0
0·1	2030	0·21	0·18	0·39	6·8	5·8	12·6
0·15	1920	0·38	0·3	0·68	12·5	9·7	22·2
0·2	1800	0·53	0·4	0·93	17·4	13·0	30·4
0·25	1700	0·67	0·48	1·15	21·7	15·6	37·3
0·3	1610	0·77	0·53	1·30	25·0	17·2	42·2
0·4	1460	0·93	0·61	1·54	30·2	19·8	50·0
0·5	1330	1·05	0·66	1·71	34·0	21·4	55·4

Table III.—Heat Loss in a 9·7 per cent. Mixture of Coal-Gas and Air. Heat of Combustion of Coal-Gas in Vessel = 10,600 calories.

Time after ignition (secs.).	Mean gas temperature (° C. abs.).	Heat loss per sq. cm. of surface.			Heat loss expressed as a percentage of the heat of combustion of the coal-gas.		
		Conduction.	Radiation.	Total.	Conduction.	Radiation.	Total.
0·18	1660	0·26	0·17	0·43	11·0	7·0	18·0
	(max. temp.)						
0·2	1650	0·31	0·2	0·51	12·8	8·3	21·1
0·25	1580	0·4	0·27	0·67	16·5	11·2	27·7
0·3	1520	0·47	0·33	0·80	19·4	13·6	33·0
0·4	1390	0·59	0·42	1·01	24·4	17·4	41·8
0·5	1310	0·67	0·46	1·13	27·7	19·0	46·7

It will be noticed that the conduction loss is from 40 to 60 per cent. greater than the radiation loss in each mixture. This applies, however, only to explosion vessels of the size used in these experiments. In much larger vessels the radiation loss per square centimetre may be greater than the conduction loss per square centimetre, for it increases with the size of the vessel,* whereas the conduction loss per unit area of wall surface is practically independent of the dimensions of the vessel.

It will be seen from the Tables that the 15 per cent. mixture has lost to the walls of the vessel 8·9 per cent. of its heat of combustion by the time it has attained its maximum pressure; of this 5·1 per cent. is due to conduction and 3·8 per cent. to radiation. The 12·4 per cent. mixture has lost at the same moment some 10 per cent. of its heat of combustion (5·5 per cent. by conduction and 4·5 per cent. by radiation). The loss at the moment of maximum pressure in the 9·7 per cent. mixture is much greater;† it amounts to about 18 per cent. of its heat of combustion, of which 11 per cent. is due to conduction and 7 per cent. to radiation.

Further information with regard to the heat lost up to the moment of maximum temperature ($\theta_{\max.}$) is set out in Table IV. It will be seen from this Table that the heat loss per square centimetre up to this moment ($H_{\max.}$) is proportional to the product of $\theta_{\max.}^{2.5}$ and the time of explosion (t_e), and that the proportion of the heat of combustion lost up to this moment

* See p. 308. It is estimated that in a vessel 70 cm. in diameter by 70 cm. in length, the radiation loss would be about the same as the conduction loss for mixtures at atmospheric density.

† This is due to its much longer explosion period. The time of explosion in the 9·7 per cent. mixture is 0·18 sec., whereas it is only 0·05 sec. and 0·08 sec. in the 15 per cent. and 12·4 per cent. mixtures respectively.

Table IV.—Heat Loss to Walls of Vessel up to Moment of Maximum Temperature.

Mixture.	Max. abs. temp. of gaseous mixture ($\theta_{\max.}$).	Time of explosion (t_e).	Heat loss in calories per sq. cm. up to max. temp. ($H_{\max.}$).	$\frac{H_{\max.}}{\theta_{\max.}^{2.5} \times t_e}$.	Proportion of heat of combustion of coal-gas lost to walls up to max. temp. ($H_{C. \max} = \frac{H_{\max.} \times 4380}{C}$).	$\frac{H_{C. \max.}}{\theta_{\max.}^{1.5} \times t_e}$.
per cent.						
15	2440	0.05	0.33	2.24×10^{-8}	0.089	1.47×10^{-5}
12.4	2050	0.08	0.31	2.08	0.10	1.36
9.7	1660	0.18	0.43	2.12	0.18	1.47
Mean values				2.15×10^{-8}		1.43×10^{-5}

($H_{C. \max.}$) is proportional to the product of $\theta_{\max.}^{1.5}$ and t_e . The experimental results indicate that $H_{\max.}$ and $H_{C. \max.}$ may be calculated for any mixture by means of the equations

$$H_{\max.} = 2.15 \times 10^{-8} \theta_{\max.}^{2.5} \times t_e$$

and

$$H_{C. \max.} = 1.43 \times 10^{-5} \theta_{\max.}^{1.5} \times t_e.$$

These equations, of course, hold only for coal-gas mixture contained in a vessel of the same size and shape as that used in these experiments and exploded at atmospheric density.*

The curves in fig. 4 and the figures in Table V show the rate of heat loss (radiation, conduction and total) in the various mixtures. It has been shown in a previous paper† that when the gaseous mixtures are exploded at atmospheric density the rate at which they lose heat by radiation per square centimetre of wall surface per second ($\dot{R}$) in the experimental vessel is approximately given by

$$\dot{R} = 1.75 \times 10^{-14} \theta^4,$$

where θ is the mean absolute temperature of the gaseous mixture. It was further shown that in a cylindrical vessel l cm. in diameter and l cm. in length that

$$\dot{R} = 0.32 \times 10^{-14} \theta^4 \sqrt{(l)}.$$

It has also been shown‡ that the rate of loss of heat by conduction per

* This is because that part of $H_{\max.}$ and $H_{C. \max.}$ which is due to radiation is dependent both upon the density and the volume of the gaseous mixture.

† 'Phil. Mag.,' January, 1920, p. 66.

‡ 'Phil. Mag.,' September, 1920, p. 326.

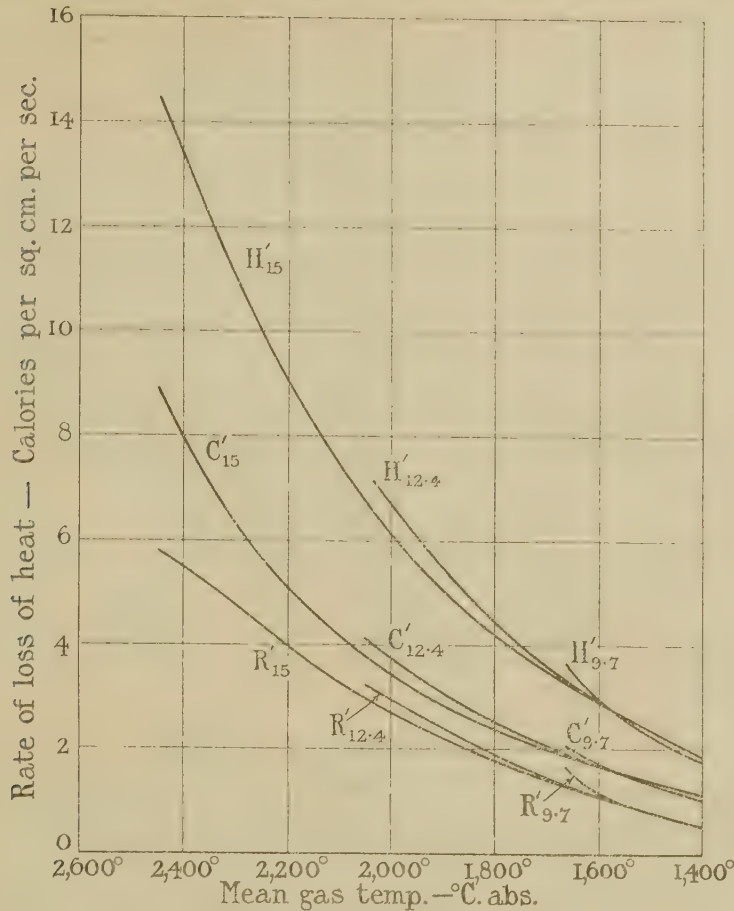


FIG. 4.—Rate of loss of heat in 15, 12.4, and 9.7 per cent. mixtures. H' curves, total heat-loss ; C' curves, loss by conduction ; R' curves, loss by radiation.

Table V.—Rate of Loss of Heat in 15 per cent., 12.4 per cent., and 9.7 per cent. Mixtures of Coal-Gas and Air.

Mean gas temperature (°C. abs.).	Rate of loss of heat. Calories per sq. cm. per sec.								
	15 per cent. mixture.			12.4 per cent. mixture.			9.7 per cent. mixture.		
	Conduction.	Radiation.	Total.	Conduction.	Radiation.	Total.	Conduction.	Radiation.	Total.
2440	8.7	5.8	14.5						
2400	7.9	5.4	13.3						
2200	5.0	3.9	8.9						
2050	3.8	2.9	6.7	4.1	3.2	7.3			
2000	3.4	2.7	6.1	3.7	2.9	6.6			
1800	2.4	1.8	4.2	2.5	1.9	4.4			
1660	1.9	1.4	3.3	1.9	1.4	3.3	2.1	1.6	3.7
1600	1.7	1.2	2.9	1.7	1.2	2.9	1.8	1.2	3.0
1400	1.2	0.7	1.9	1.2	0.7	1.9	1.1	0.7	1.8

square centimetre of wall surface per second ($\dot{C}$) is approximately given by

$$\dot{C} = 4 \times 10^{-13} (\theta - \theta_w)^4$$

for temperatures above 2000° C. abs. and by

$$\dot{C} = 7 \times 10^{-10} (\theta - \theta_w)^3$$

for temperatures below 2000° C. abs.; where $(\theta - \theta_w)$ is the difference between the temperature of the gaseous mixture and that of the walls of the explosion vessel. It is probable that $\dot{C}$ is independent of the size of the vessel and the above formulæ, therefore, probably hold for a vessel of any dimensions.

The rate of total heat loss per square centimetre of wall surface per second ($\dot{H}$) in a cylindrical vessel l cm. by l cm., containing mixtures of coal-gas and air at atmospheric density is therefore given approximately by

$$\dot{H} = 4 \times 10^{-13} (\theta - \theta_w)^4 + 0.32 \times 10^{-14} \theta^4 \sqrt{l}$$

for temperatures above 2000° C. abs. and by

$$\dot{H} = 7 \times 10^{-10} (\theta - \theta_w)^3 + 0.32 \times 10^{-14} \theta^4 \sqrt{l}$$

for temperatures below 2000° C. abs.

Internal Energy of the Gaseous Mixtures.

From the experimental results described in the preceding section an estimate of the internal energy of the gaseous mixtures at various temperatures may be obtained. The internal energy at any moment is equal to the heat of combustion of the coal-gas originally in the vessel less the heat loss to the walls of the vessel up to that moment. The values of the internal energy of the different mixtures at various temperatures derived in this way are given in Tables VI, VII, and VIII.

The figures in column 4 of the Tables have been taken from the curves in figs. 1, 2, and 3. They give the total heat loss (*i.e.*, the radiation and the conduction losses) per square centimetre of wall surface when the gas temperatures have fallen to the values shown in column 2. The figures in column 5 represent the total heat loss over the entire surface of the vessel. They have been obtained by multiplying the figures in column 4 by 4380, which is the area in square centimetres of the interior surface of the explosion vessel. The figures in column 6 give the internal energy (reckoned from atmospheric temperature) of the gaseous mixtures in the explosion vessel at the various temperatures given in column 3. These values have been calculated by subtracting the total heat loss from the heat of combustion of the coal-gas. The volume of the gaseous mixture in the vessel, measured at

Table VI.—Internal Energy of 15 per cent. Mixture of Coal-Gas and Air after Explosion. Heat of Combustion of Coal-Gas in Vessel = 16,300 calories.

Composition of Mixture after Combustion $\left\{ \begin{array}{l} \text{N and O...71.5 per cent.} \\ \text{CO}_2 \text{ 8.5} \text{ }'' \\ \text{H}_2\text{O} \text{ 20.0} \text{ }'' \end{array} \right.$

Time after ignition (secs.).	Mean gas temperature (° C. abs.).	Mean gas temperature (° C.).	Heat loss calories per sq. cm. (H).	Total heat loss over whole surface of vessel = $H \times 4380$ (calories).	Internal energy of gaseous mixture in vessel reckoned from atmospheric temperature = $16,300 - H \times 4380$ (calories).	Internal energy of gaseous mixture per gramme-molecule reckoned from 100° C. (calories).
0	—	15	0	0	(16,300)	(17,550)
0.05	2440 (max. temp.)	2170	0.33	1,450	14,850	15,950
0.06	2400	2130	0.52	2,280	14,020	15,050
0.1	2200	1930	0.97	4,250	12,050	12,900
0.15	2000	1730	1.34	5,870	10,430	11,100
0.22	1800	1530	1.66	7,280	9,020	9,570
0.3	1600	1330	1.96	8,600	7,700	8,100
0.42	1400	1130	2.27	10,000	6,300	6,650

Table VII.—Internal Energy of 12.4 per cent. Mixture of Coal-Gas and Air after Explosion. Heat of Combustion of Coal-Gas in Vessel = 13,500 calories.

Composition of Mixture after Combustion $\left\{ \begin{array}{l} \text{N and O...76.6 per cent.} \\ \text{CO}_2 \text{ 7.0} \text{ }'' \\ \text{H}_2\text{O} \text{ 16.4} \text{ }'' \end{array} \right.$

Time after ignition (secs.).	Mean gas temperature (° C. abs.).	Mean gas temperature (° C.).	Heat loss calories per sq. cm. (H).	Total heat loss over whole surface of vessel = $H \times 4380$ (calories).	Internal energy of gaseous mixture in vessel reckoned from atmospheric temperature = $13,500 - H \times 4380$ (calories).	Internal energy of gaseous mixture per gramme-molecule reckoned from 100° C. (calories).
0	—	15	0	0	(13,500)	(14,320)
0.08	2050 (max. temp.)	1780	0.31	1,360	12,140	12,950
0.11	2000	1730	0.48	2,100	11,400	12,050
0.2	1800	1530	0.93	4,070	9,430	9,900
0.3	1600	1330	1.31	5,740	7,760	8,150
0.45	1400	1130	1.63	7,150	6,350	6,650

Table VIII.—Internal Energy of 9·7 per cent. Mixture of Coal-Gas and Air after Explosion. Heat of Combustion of Coal-Gas in Vessel = 10,600 calories.

Composition of Mixture after Combustion $\left\{ \begin{array}{l} \text{N and O} \dots 81\cdot6 \text{ per cent.} \\ \text{CO}_2 \dots \dots 5\cdot5 \quad , \\ \text{H}_2\text{O} \dots \dots 12\cdot9 \quad , \end{array} \right.$

Time after ignition (secs.).	Mean gas temperature (° C. abs.).	Mean gas temperature (° C.).	Heat loss calories per sq. cm. (H).	Total heat loss over whole surface of vessel = $H \times 4380$ (calories).	Internal energy of gaseous mixture in vessel reckoned from atmospheric temperature = $10,600 - H \times 4380$ (calories).	Internal energy of gaseous mixture per gramme-molecule reckoned from 100° C. (calories).
0	—	15	0	0	(10,600)	(11,050)
0·18	1660 (max. temp.)	1390	0·43	1,880	8,720	9,050
0·24	1600	1330	0·61	2,670	7,930	8,200
0·31	1500	1230	0·82	3,600	7,000	7,200
0·4	1400	1130	0·98	4,300	6,300	6,450

normal temperature and pressure, is 21 litres, and the internal energy per gramme-molecule (taken as 22·25 litres) is therefore equal to the internal energy of the gaseous mixture in the vessel multiplied by $\frac{22\cdot25}{21(1-x)}$, where x is the contraction of volume* which takes place during combustion. The figures in column 7 are those in column 6 multiplied by this factor, less about 350 calories, which is the internal energy per gramme-molecule between atmospheric temperature and 100° C. The figures in column 7, therefore, give the internal energy of the gaseous mixtures per gramme-molecule reckoned from 100° C.

The data in these tables have been plotted in fig. 5. The curves show the internal energy (reckoned from 100° C.) per gramme-molecule of the different mixtures at various temperatures. The chain-dotted curves show the values of the internal energy of the various mixtures used in my experiments, as calculated from the specific heat values determined by Holborn and Henning. The dotted curve shows Clerk's values for a mixture which is of nearly the same composition as the 9·7 per cent. mixture used in these experiments.† Clerk's values and those of Holborn and Henning and mine are compared in Table IX.

It will be seen that Clerk's results and mine for the weak mixture in the later stages of cooling are very nearly the same, but the values of Holborn

* This is of the order of 3 per cent.

† The composition of Clerk's mixture is:—N and O, 83 per cent. ; CO₂, 5 per cent. ; H₂O, 12 per cent.

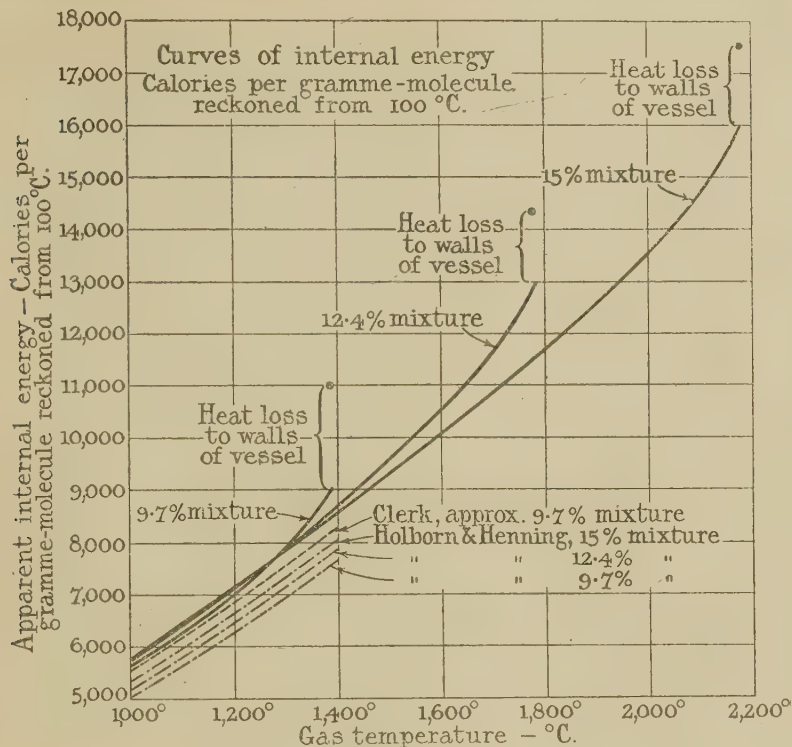


FIG. 5.

Table IX.—Internal Energy of the Gaseous Mixtures according to Holborn and Henning, Clerk, and the Explosion Experiments described in the present paper.

Internal energy reckoned from 100° C.—calories per gramme-molecule.							
Mean gas temperature. (° C.)	15 per cent. mixture.		12.4 per cent. mixture.		9.7 per cent. mixture.		
	Explosion experiments.	Holborn and Henning.	Explosion experiments.	Holborn and Henning.	Explosion experiments.	Holborn and Henning.	Clerk.
2170*	16,000						
2000	13,600						
1800	11,700						
1780†	11,500	—	12,900				
1600	10,100	—	11,500				
1400	8,600	8,100	8,700	7,850			
1390‡	8,500	8,000	8,600	7,750	9,050	7,600	8,200
1200	7,200	6,700	7,200	6,500	7,050	6,300	6,900
1000	5,800	5,300	5,800	5,150	5,600	5,000	5,500

* (Max. temp., 15 per cent. mixture.) † (Max. temp., 12.4 per cent. mixture.)
‡ (Max. temp., 9.7 per cent. mixture.)

and Henning are considerably lower. The absolute values of the internal energy, as determined by my experiments, are subject to a possible error of some magnitude in that the conduction loss, having been determined in one position only, may not give a true average for the whole vessel. They cannot be used, therefore, to decide between Clerk's results and those of Holborn and Henning.* But the closeness between my results in the later stages of cooling and these results lends considerable confidence to the view that they show with a considerable degree of accuracy the variation in the internal energy values with temperature and time after ignition, and it is to a discussion of this that the remainder of the paper will be devoted.

The most noticeable feature of the internal energy curves is their rapid variation with temperature in the neighbourhood of the maximum temperatures and in the initial stages of cooling. It will be seen that the weaker mixtures in the initial stages of cooling possess a much greater apparent internal energy than the stronger mixtures when they have cooled to the same temperatures as the weaker mixtures have in this epoch—even though the stronger mixtures contain a larger proportion of CO_2 and steam than the weaker mixtures. This is also clearly shown by the curves in fig. 6,† which are the differentials of the internal energy curves in fig. 5 with respect to temperature. They show the rate of change of internal energy with temperature, or in other words, the instantaneous values of the volumetric heat (or rather of the *apparent* volumetric heat) of the various gaseous mixtures. In the case of the weaker mixtures the apparent volumetric heat values at maximum temperature and in the initial stages of cooling are very much greater than those of the stronger mixtures when they have cooled to the same temperatures as the weaker mixtures have in this epoch; indeed, in the neighbourhood of the maximum temperatures of the weaker mixtures the apparent volumetric heat of these mixtures is about three times as great as that of the stronger mixtures.

It is difficult to account for these results except in terms of continued combustion.‡ They cannot be explained in terms of the large temperature

* It is the general impression that the true values lie somewhere between Clerk's values and those of Holborn and Henning. (See 'First Report of the British Association Committee on Gaseous Explosions.')

† There is some uncertainty as to the exact values of the apparent volumetric heat values in the immediate neighbourhood of the maximum temperatures, and the curves in fig. 6 have accordingly not been continued to cut the dotted lines of maximum temperatures. They would appear to be between 20 and 30 calories per gramme-molecule at these temperatures.

‡ Hopkinson concluded from his experiments with platinum wires ('Roy. Soc. Proc.,' A, vol. 77, p. 409) that combustion once initiated in any part of the gaseous mixture was almost instantaneously completed. I am doubtful, however, whether the state of the gas

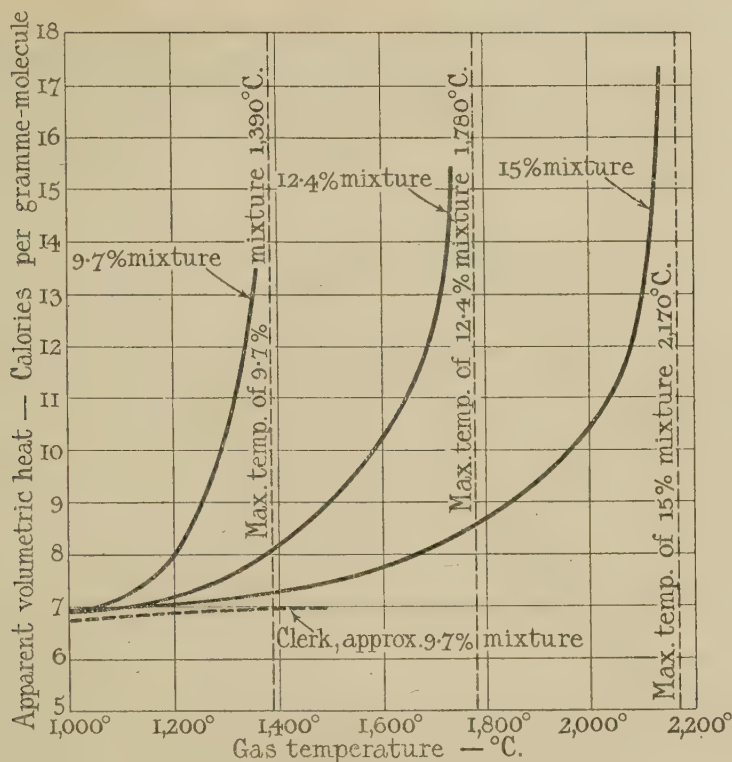


FIG. 6.—Volumetric heat of the various mixtures.

differences which exist in the gaseous mixtures at the moment of attainment of maximum temperature and the increase of the volumetric heat with temperature, for its rate of increase at these high temperatures is far too small to account to any appreciable extent for the results. Nor is it likely that they can be explained in terms of an excess of intra-molecular energy in this epoch, for it is highly probable that the rate of transfer of energy between the internal and the translational degrees of freedom of the molecules is extremely rapid at the high explosion temperatures.

Assuming then, as seems highly probable, that the apparent internal energy at maximum temperature and in the initial stages of cooling consists partly (and mainly) of thermal energy and partly of available chemical energy, an estimate of the amount of chemical energy in the gaseous mixtures in this epoch may be made from the curves. Such an estimate is obtained by subtracting from the apparent internal energy values of the weaker mixtures the internal energy values given by the curve for the strong mixture when near the wires was representative of that throughout the mass of the gas. Surface combustion probably speeded up the burning of the gaseous mixture in the immediate neighbourhood of the wires.

equilibrium has been attained, after making, of course, an allowance for the difference in composition of the mixtures. Estimates obtained in this way for the various mixtures at the moment of maximum temperature are given in Table X. The amount of heat lost to the walls of the explosion vessel up to this moment is also given in the Table.

Table X.—Distribution of Energy per Gramme-molecule at the Moment of Maximum Temperature.

Mixture.	Heat of combustion.	Internal thermal energy.	Available chemical energy.	Heat loss to walls of explosion vessel.
15 per cent.	17,600 100	14,200 81 per cent.	1,800 10 per cent.	1,600 9 per cent.
12·4 per cent. ...	14,350 100	11,200 78 per cent.	1,700 12 per cent.	14,500 10 per cent.
9·7 per cent. ...	11,050 100	8,000 72·5 per cent.	1,050 9·5 per cent.	2,000 18 per cent.

It will be seen from the Table that about 10 per cent. of the coal-gas originally in the vessel appears to be unburnt in each mixture at the moment of maximum temperature. Maximum temperature and pressure would therefore appear to be reached when about 90 per cent. of the coal-gas has been burnt. The proportion of the heat of combustion in the form of thermal energy at the moment of maximum temperature varies from about 80 per cent. in the 15 per cent. mixture to about 72 per cent. in the 9·7 per cent. mixture; and the heat loss to the walls up to this moment ranges from about 9 per cent. of the heat of combustion in the 15 per cent. mixture to about 18 per cent. in the case of the 9·7 per cent. mixture.

These results may be summarised in the form of an equation. Let

C be the heat of combustion of the coal-gas in the experimental vessel,
 $c_{\max.}$ be the proportion of the coal-gas unburnt at the moment of maximum temperature,

$E_{\theta_0, \theta_{\max.}}$ the internal thermal energy (reckoned from atmospheric temperature) of the gaseous mixture in the experimental vessel at the moment of maximum temperature,

and $H_{\max.}$ the heat loss per square centimetre of wall surface up to the moment of maximum temperature.

Then

$$C = E_{\theta_0, \theta_{\max.}} + c_{\max.} C + 4380 H_{\max.},$$

and therefore,

$$\begin{aligned} E_{\theta_{\sigma}, \theta_{\max.}} &= 0.9C - 9.4 \times 10^{-5} \theta_{\max.}^{2.5} \times t_e \\ &= (0.9 - 1.43 \times 10^{-5} \theta_{\max.}^{1.5} \times t_e) C, \end{aligned}$$

since $C_{\max.} = 0.1$ approximately, $H_{\max.} = 2.15 \times 10^{-8} \theta_{\max.}^{2.5} \times t_e$

and $H_{C, \max.} = 1.43 \times 10^{-5} \theta_{\max.}^{1.5} \times t_e$.*

The internal (thermal) energy (reckoned from atmospheric temperature) per gramme-molecule is obtained by multiplying the values for $E_{\theta_{\sigma}, \theta_{\max.}}$ calculated by means of the formulæ given above by the factor $\frac{22.25}{V_0(1-x)}$

where V_0 is the volume of the gaseous mixture before inflammation, measured at normal temperature and pressure, and x is the contraction of volume which takes place on combustion.

These formulæ are useful in that by means of them it is possible to calculate the internal (thermal) energy at the moment of maximum temperature from data which may be furnished by pressure-time curves. It should be pointed out that they are strictly applicable only to coal-gas and air mixtures which are—

(i) Contained in a vessel of the same shape and size as that used in these experiments and exploded at atmospheric density, because the radiation part of the heat loss, $H_{\max.}$, varies both with the size and shape of the containing vessel, and also with the density of the gaseous mixture; and

(ii) Of approximately the same chemical composition as the mixtures used in the experiments, so that the rate of combustion and time of explosion, t_e , are similar.

An examination of the volumetric heat curves in fig. 6 seems to indicate that combustion is proceeding in appreciable volume in the 15 per cent. mixture until it has cooled to about 1400°C . (that is for roughly 0.3 second after ignition, or 0.25 second after maximum pressure). After this temperature has been reached the shape of the volumetric heat curve indicates that the gaseous mixture has practically attained chemical equilibrium. In the 12.4 per cent. mixture, combustion seems to be going on until it has cooled to below 1200°C . (that is, about 0.4 second after ignition, or 0.3 second after maximum pressure); and, in the 9.7 per cent. mixture, some burning seems to be going on after it has cooled to below 1100°C . (that is, about 0.5 second after ignition, or 0.3 second after maximum pressure).

* See p. 308.

Summary.

In the first section of this paper heat-loss measurements by conduction and by radiation made during the explosion and subsequent cooling of mixtures of coal-gas and air of various strengths have been combined. The heat loss by conduction was found to be from 40 per cent. to 60 per cent. greater than the loss by radiation in the experimental vessel. In a vessel rather more than twice as large the radiation loss would have been about equal to the conduction loss, and in a still larger vessel it would have been greater. Formulæ have been built up by means of which the total heat loss up to the moment of maximum pressure, and the rate of heat loss at any temperature during cooling may be calculated from data which may be obtained from the pressure-time curves.

In the second section of the paper the heat-loss measurements have been applied to the estimation of the internal energy and the volumetric heat of the different mixtures at various temperatures after explosion. An examination of the internal energy and volumetric heat curves so obtained indicates that at the moment of maximum pressure about 10 per cent. of the heat of combustion of the coal-gas in each mixture has not been converted into thermal energy, and that after-burning continues for at least 0.25 second after maximum pressure has been attained.

It is believed that these results show that the energy of combustion of the coal-gas originally in the vessel is distributed at the moment of maximum temperature as follows:—

(i) *Internal (thermal) energy*: From about 72 per cent. of the heat of combustion of the coal-gas in a 9.7 per cent. mixture to about 80 per cent. in a 15 per cent. mixture.

(ii) *Available chemical energy*: About 10 per cent. in each mixture.

(iii) *Heat loss to walls of vessel*: From about 10 per cent. in a 15 per cent. mixture to about 18 per cent. in a 9.7 per cent. mixture.

*Address of the President, Sir J. J. Thomson, O.M., at the
Anniversary Meeting, November 30, 1920.*

The list of Fellows on the Home List who have died since the last Anniversary Meeting includes the names of

Lord Walsingham.	Prof. J. A. McClelland.
Sir William Osler.	Mr. R. Messel.
Sir Thomas Fraser.	Mr. S. Ramanujan.
Mr. C. E. Groves.	Mr. L. Doncaster.
Prof. Charles Lapworth.	Prof. J. Perry.
Prof. Emerson Reynolds.	Sir Norman Lockyer.
Capt. Creak.	Mr. J. G. Baker.

While on the Foreign List we have lost

Prof. Schwendener.	Prof. Pfeffer.
Prof. Voigt.	Prof. Timiriazeff.
Prof. Rydberg.	Prof. Hering.
Prof. Righi.	

Our obituary notices contain detailed accounts of the achievements of these distinguished men; to-day I must content myself with the briefest possible reference to the most conspicuous of their contributions to Science.

LORD WALSINGHAM was a traveller and a keen sportsman, a distinguished entomologist, to whom the Natural History Museum owes a large collection of microlepidoptera.

SIR WILLIAM OSLER, by birth a Canadian, was for many years one of the leaders of Medical Science in America, where he did much to establish the great fame of the Johns Hopkins School of Medicine; when in 1905 he came to Oxford as Regius Professor of Medicine, he succeeded in winning, to a quite remarkable degree, the confidence and esteem of that University. He was eminent as a practitioner, as a teacher, and as a writer, and had a keen sympathy with literature as well as with Science.

SIR THOMAS FRASER was Professor of Materia Medica in the University of Edinburgh for forty-three years, and was one of the pioneers of experimental Pharmacology.

MR. C. E. GROVES will long be remembered in connection with the invaluable Journal of the Chemical Society, with which he was associated, first as sub-editor and then as editor, for more than twenty years.

PROF. CHARLES LAPWORTH, the distinguished Professor of Geology at Birmingham, brought the study of the palæozoic rocks to the level of an exact science.

Prof. EMERSON REYNOLDS for his success as a teacher of Chemistry and for the importance of his discoveries in that Science. He added much to our knowledge of the properties of silicon and beryllium.

Captain CREAK was a veteran naval officer who had done much to improve the compass for Admiralty purposes and was an authority on the magnetism of ships and on terrestrial magnetism.

Physical science lost much by the death, at an early age, of my old pupil, Prof. J. A. McCLELLAND, who was one of the first research students at the Cavendish Laboratory. He had done valuable work on the passage of electricity through gases; he was a very successful professor at the Royal University of Ireland, and an energetic member of the advisory Committee for Scientific and Industrial Research.

Mr RUDOLPH MESSEL was distinguished for his success and originality in industrial Chemistry. He left to us by his will one of the most munificent bequests ever received by the Society.

Mr. S. RAMANUJAN, the first native of India to be elected a Fellow of our Society, was in some respects one of the most interesting names in the history of Mathematics. Self-taught as a mathematician, he sent, in 1913, a letter to Prof. G. H. Hardy, enunciating more than one hundred theorems; though not all of these were true, it was evidently the work of one who had a genius for Mathematics. Steps were taken to bring him to Cambridge, and he entered Trinity College in 1914; in the following three years he published twenty papers on pure Mathematics, some of them of great importance. Afterwards, his health broke down and he returned to India, where he died this year. He was a fellow of Trinity College: the first native of India who had ever won this distinction. Prof. G. H. Hardy has stated that "it is not extravagant to suppose that he might have become the greatest mathematician of his time."

The death of LEONARD DONCASTER at the early age of forty-two has cut short a career of exceptional promise and distinction. He took an active part in the early stages of Mendelism in this country, he made important contributions to the subject of sex-determination, and was a leader in cytology in this country. He was a very successful teacher, whose death Prof. Herdman has stated to be nothing else than a calamity to Liverpool University.

The loss of Prof. PERRY leaves a very noticeable gap in scientific circles. His enthusiasm and originality were as stimulating as they were delightful, and discussion never flagged when Perry was present. A pupil of Andrews and an assistant to Lord Kelvin, he went early in life to teach Science to the Japanese, and, in collaboration with Ayrton, poured out in the "eighties" a

flood of researches on electrical subjects, so copious as to threaten to transfer the centre of electrical science to Japan. In conjunction with Armstrong and Ayrton, he established and determined the policy of Finsbury Technical College, an institution whose methods were as original as they were successful. He led a crusade on the proper way to teach Mathematics to students of Engineering, which has had a permanent, and, on the whole, a salutary effect on the methods adopted for that purpose. He had a long and intimate connection with the British Association, for which he was Treasurer for sixteen years. He did much for science by his personality, as well as by his researches.

Sir NORMAN LOCKYER had been a Fellow of the Society for more than fifty years, having been elected in 1869, immediately after the discovery of his method for revealing and studying the red flames in the solar atmosphere when the sun is not eclipsed. He took a very prominent part in the progress of Solar Physics for more than fifty years. He was fertile in ideas as well as in experiments, some of these have had much influence on the progress of Science, and even those which have not been confirmed by later experiments have aided the progress of knowledge by stimulating research and suggesting experiments which otherwise might not have been tried. He was the chief of no less than eight solar eclipse expeditions and organised the programme of several others. He was Professor of Astronomical Physics at the Royal College of Science and Director of the Solar Physics Observatory at South Kensington from 1885 to 1913, and when the observatory was transferred to Cambridge he established one of his own near Sidmouth. Among his other achievements is that of linking up Astronomy with Archæology, and thereby determining the date of construction of Stonehenge. He was indefatigable in urging the importance of Science for the welfare of the Nation and the necessity for the Government to assist and promote research and University Education. Last but not least are the services which he rendered to Science as Editor of 'Nature.'

Mr. J. G. BAKER, the veteran botanist, had been a Fellow of the Society for more than forty years, he had done splendid work for the herbarium at Kew and for systematic Botany.

Of those deceased on the Foreign list Dr. SCHWENDENER was the discoverer of the true nature of lichens and the founder of the study of the physiological anatomy of plants. Prof. VOIGT of Göttingen was an indefatigable worker at mathematical physics, the leading authority on the physics of crystals, a man of wide sympathies and an accomplished musician. Prof. RYDBERG's discovery of the various series in the lines of the spectra of various elements has had a profound effect on the development of spectroscopy. Prof. PFEFFER

was a great botanist whose researches on osmotic pressure made his name as familiar to physicists as it was to botanists. Prof. TIMIRIAZEFF was a botanist whose book on the "Life of the Plant" is a model for the statement of profound scientific truths in terms so clear and simple and eloquent as to be delightful to the ordinary reader. Prof. HERING was a physiologist well known for his work on colour blindness, while Prof. RIGHI had made important contributions to our knowledge of electrical waves and the passage of electricity through gases. He was one of the leading spirits in the great renaissance of scientific research in Italy, which has been so conspicuous a feature in its recent history.

To turn now from those we have lost to those we have gained. On January 22 we were honoured by the presence, at a Special Meeting of the Society, of H.R.H. the Prince of Wales, who was then admitted into the Society. The accession to our list of Fellows of the Heir to the Throne is always regarded as a great honour to the Society, in this case the honour was exceptionally great, as we received one who, in addition to the prestige of his exalted position, has a splendid record of conspicuous and vital services to the Empire. Mr. H. A. L. Fisher and Sir J. G. Frazer have been elected Fellows of the Society under Statute XII.

The year has been memorable for the magnitude of the bequests which have been made to the Society: Dr. Messel, our late Fellow, has left to the Society a legacy which, it is estimated, will exceed £70,000, thus showing his goodwill to the Society and his appreciation of the value of pure science; this is the largest bequest ever made to the Society for general purposes. Under the will of Miss Fullarton we shall receive a substantial endowment for the Fullarton Fund for Studentships in Medical Science, and within the last few weeks we have received notice that under the will of Mr. Smithson the Society has been left the reversion of an estate which, it is estimated, will amount to between £18,000 and £20,000. In the case of the Messel and Smithson bequests, the Society is left some freedom with regard to the purposes for which they can be applied, a fact which greatly enhances their value to the Society. The amount received this year by bequest is the greatest on record—may that record soon be broken.

Our Assistant Secretary, Dr. Deller, has been appointed Academic Registrar to the University of London; we regret his departure, and he will carry with him to his new office the good wishes of the Fellows of our Society.

The rise in the cost of paper, printing, and binding has caused a large increase in the cost of publishing our 'Proceedings' and 'Transactions,' in spite of the fact, that owing to the interruption of research caused by the

war, the number of papers communicated to the Society has not yet reached its normal value, it is, however, rapidly doing so and we must, I think, be prepared to face a continual increase in the cost of publication for the next few years. I am not sure that the majority of our Fellows realise the cost of publication of some of our papers. I may perhaps bring this home to them by mentioning that we have now one paper recommended for publication, which it is estimated will cost £500 to produce, and though this is exceptional, there are many papers which cost more than £100. Figures, such as these, show how important it is that contributors of papers should help the Society by rigid economy in the number of plates and by making their papers as concise as is consistent with clearness. Prolixity of statement is one of the most difficult things to combat; the referees can suggest the omission of irrelevant and superfluous matter—it is much more difficult for them to take action when the matter is relevant, but could be expressed in half the number of words required by the author.

It was said of one eminent man that he never used one word when forty would do; this quality may be useful under some circumstances, but it would not, I think, be appreciated by the officers of a Society that had to find the funds for the publication of papers by an author with this characteristic.

It has been urged that the days of publication of scientific papers through a Society are past, and that the proper vehicle of publication is a journal, such for example, as the 'Philosophical Magazine'; from the point of view of the dissemination of knowledge, this plan possesses advantages with regard to finance and convenience. These advantages would, in my opinion, be dearly purchased, for I think the reading of papers assists Science by making it more human, by bringing men who are working at a subject into contact with others who are working at it, from different, possibly from antagonistic points of view; again, I think having to read a paper before a Society tends to make an author take more pains to make it intelligible to those who are not specialists in the subject.

I do not mean to imply that all papers should be read before or even communicated to a Society—there are many that are best published independently—there is room for both methods of publication. It is important, however, that those published by a Society should be as accessible and have as wide a circulation as those published in other ways. In this respect I think there is room for reform; the circulation of our papers is not so large as it ought to be. No doubt, this is to some extent due to the fact that some of our publications include papers on many different subjects. 'Proceedings, B,' for example, contains papers on Botany, Physiology,

Zoology, and Geology, and there are some who, though they would wish to possess the papers on one of these subjects, cannot afford the price required to pay for the other subjects as well. This, however, cannot be the only reason, for it does not apply to 'Proceedings, A,' which are as homogeneous as the 'Philosophical Magazine.' Perhaps the sale might be improved if the publications came out at a fixed date and at a fixed price, so as to make it easier for the bookseller to handle them.

I think that some improvement in our sales might possibly be effected and science benefited if there were some organisation, private or otherwise, for the sale of separate papers. The formation of a library, to include all papers on one of the great branches of science such as physics, requires a longer purse and more bookshelves than most are able to afford. But there are many, I think, who would like and could afford to form a fairly complete collection of the literature of one or more of the sub-divisions of the subject in which they are especially interested—say, for example, electrical waves or low temperature research. As lists of the papers in these sub-divisions are published at regular intervals by various agencies, it ought not to be difficult to arrange for the distribution of the separate papers if these could be obtained from the Societies.

In a few minutes I shall cease to be President of the Society. I should like to spend these in thanking the Fellows and Officers for the kindness, goodwill, and forbearance which they have extended to me in such full measure during my term of office. The position of President of the Royal Society would, under all circumstances, be one of great honour. I have found it, in addition, one of great pleasure; that it has been so is due entirely to your kindness. I wish to thank my colleagues, both those in office now and their predecessors, Sir Alfred Kempe, Sir Arthur Schuster, and Dr. Scott, who for five exceptionally arduous and trying years have borne so patiently with my many shortcomings, who have helped me in every way in their power, and, what I value no less highly, have granted me their sympathy and friendship. My thanks are due to the Assistant Secretaries, Mr. Harrison and Dr. Deller, and to every member of the staff. To the kindness of the Fellows, I owe it that I take away with me, when I retire from office, recollections of unmixed pleasure, recollections which will be a solace and joy to me for the rest of my life.

I congratulate and welcome my successor. I think I shall not be accused of rash speculation if I assume that he is a man of preeminent distinction in Physiology, and one who has won the confidence and esteem of workers in every branch of Science.

We now proceed to the distribution of the Medals.

The Copley Medal is awarded to Dr. Horace T. Brown in recognition of his work on the chemistry of carbohydrates, on the assimilation of atmospheric carbon dioxide by leaves, and on gaseous diffusion through small apertures.

As was the case with Pasteur, so with Horace Brown; problems and difficulties arising out of a branch of the fermentation industry supplied the incentive to investigations which are of fundamental importance in Chemistry and Botany.

His earliest investigations dealt with one of the diseases of beer, and in 1871, at a period when modern bacteriological technique was unknown, he gained a complete knowledge of the life-history and chemical activities of *Saccharobacillus Pastorianus*, which at that time was responsible for most of the trouble met with in beer during maturation, and devised means to combat the waste caused by this organism.

The year 1877 marked the commencement of his exhaustive study of the chemistry of starch, which led to the publication of a series of papers dealing with the products of the hydrolysis of starch by diastase—wherein it is shown that the action may be viewed as involving the successive removal of maltose from dextrans of diminishing complexity—the molecular weight of starch and the structure of the starch molecule.

In 1885 his attention was turned to the study of the chemical and physical changes involved in the conversion of barley into malt, with the result that in 1890 he was in a position to give in his paper, entitled "Researches on some of the *Gramineae*," an explanation of the chemical and morphological changes which occur in the barley grain during the early stages of germination. This investigation, concerned mainly with the transformation and migration of the reserve carbohydrate constituents of the grain, was followed by one no less remarkable, in which he traced the relation of the sugars and starch existing in the leaves of certain plants from their inception to their translocation. The paper embodying an account of this research was published in 1893 under the title "Contribution to the Chemistry and Physiology of Foliage Leaves."

A few years later the study of the changes occurring in the green leaf during photosynthesis was extended to an investigation of difficulties connected with the absorption of carbon dioxide through the stomata of the leaf, which was found to be many times greater than expected from the operation of the law of gaseous diffusion as then understood.

In his paper on "The Principles of Diffusion, their Analogies and Applications," published in 1918, he shows how important are the results which may accrue to physical and biological science from a continued study and application of the principles of diffusion.

The Rumford Medal is awarded to Lord Rayleigh.

Lord Rayleigh is distinguished for his researches into the properties of gases at high vacua, and his work has opened the way to many valuable investigations.

Some years ago he made a number of interesting observations on the afterglow in various gases noticeable after the cessation of an electric discharge, and these led, in 1911, to his Bakerian Lecture on the "Afterglow of Nitrogen." The investigation thus started has proved the subject of much of his recent work, and in a series of most valuable papers he has studied the properties of the gas in which this afterglow is visible. This work has continued almost up to the present time; the papers show great experimental skill, the results are confirmed by numerous experiments, and the whole series constitute a very real addition to knowledge.

Quite recently he has published a new series of papers, culminating in the Bakerian Lecture of the current year. These deal with a subject which was investigated mathematically by his distinguished father nearly fifty years ago.

Our late President then showed how the blue of the sky was caused by the scattering of light by small particles in the atmosphere; his son has given a convincing demonstration of this in his paper published in February of 1918, on the "Scattering of Dust-free Air; Reproduction of the Blue Sky," and in those which have followed.

A Royal Medal is awarded to Prof. Godfrey Harold Hardy.

Prof. Hardy is well known both in this country and on the Continent for his researches in pure mathematics, particularly in the analytic theory of numbers and allied subjects. Immediately after taking his degree at Cambridge he engaged in a series of researches on the theory of functions of a real variable, from which results of the greatest importance and generality were obtained, at first by himself alone and later in collaboration with Mr. J. E. Littlewood. Perhaps his most remarkable work is his more recent work on Partitions, carried out in collaboration with the late Mr. S. Ramanujan, especially a paper on "Asymptotic Formulæ in Combinatory Analysis" ('Proc. Lond. Math. Soc.'), in which a system of approximations are obtained for $p(n)$, the number of unrestricted partitions of n and associated functions. The ingenuity of the method and the accuracy of the results are equally remarkable. For $p(200)$ the authors' approximate formula gives the value 3,972,999,029,388·004, from which the true value differs by 0·004, an error of 1 in 10^{15} .

Among the more important researches of which Prof. Hardy is sole author may be mentioned papers on Dirichlets' Divisor Problem, on the representa-

tion of numbers as the sum of n squares, on the roots of the Riemann ζ -function, and on non-differentiable functions.

A Royal Medal is awarded to Dr. William Bateson.

Dr. Bateson is universally recognised as a leading authority on genetics and has done more than anyone else to put that branch of inquiry on a scientific basis. The work that stands to his name is, however, but a fraction of that which he has inspired wherever biological research is prosecuted. The following is a record of his work during the last 10 years.

In conjunction with Prof. Punnett he worked out in detail one of the earliest cases of sex-linked inheritance. The general principle involved, that one sex is homozygous and the other heterozygous for a definite sex factor, is now generally accepted by geneticists. This principle was first stated by these authors in 1908. ('Journ. of Genetics,' 1910.)

Peculiar association of genetic factors in gametogenesis had previously been discovered by the same authors and described under the terms "coupling" and "repulsion." In 1911 they published two papers ('Proc. Roy. Soc.' and 'Journ. of Genetics'), which proved that these phenomena are part of a more general phenomenon of linkage, the orderly nature of which was pointed out. Since these papers appeared the phenomenon has been shown by various workers to be a wide-spread one, both in animals and plants; and during the past few years it has formed the basis of striking advances in genetical studies through the work of American observers on the favourable material of the little fruit fly, *Drosophila*.

Three papers by Bateson and C. Pellew ('Journ. of Genetics,' 1915, and 'Proc. Roy. Soc.'—*ibid.*, 1920) record a discovery of high interest and importance, viz., that the germ cells of the same plant may vary in their genetic properties. It is further pointed out that the variation proceeds in an orderly way from the base of the plant to the apex. The conception is a novel one, and is bound to have great influence on the development of genetical theory.

A paper by Bateson and Ida Sutton ('Journ. of Genetics,' 1919) records the discovery that in *Begonia Davisii*, a genuine wild species, the ovules bear the factor for single flowers, while the pollen is genetically double. The paper is a striking contribution to a principle insisted on by Bateson for many years, viz., that the male and female sides of a hermaphrodite plant may vary in their genetical properties.

The Davy Medal is awarded to Mr. Charles Thomas Heycock, who in collaboration with the late Mr. F. H. Neville published a remarkable series

of papers, all characterised alike by great experimental skill and originality, as well as by concise yet simple mathematical treatment. The molecular complexity of metals when dissolved in other metals, the composition and constitution of binary and ternary alloys, and the part which the eutectics play during the cooling of a complex alloy were clearly revealed, not only by freezing point methods, but by a most ingenious method of chilling, as well as by etching by means of many new reagents.

These researches have added very greatly, not only to our theoretical knowledge and conceptions, but have been of the greatest importance to industrial metallurgy in many directions.

The Darwin Medal is awarded to Prof. Roland Harry Biffen.

Prof. Biffen has worked out the inheritance of practically all the obvious characters of wheat and barley. Perhaps his best-known work is that on the inheritance of strength in wheat and on the inheritance of susceptibility and resistance to yellow rust in wheat.

Biffen has broken entirely new ground in his work on the inheritance of disease. The reason why he has succeeded in both these difficult problems, while others have failed, is that he possesses quite extraordinary imaginative insight and powers of observation. Not only is he a capable investigator, but he has proved himself to be a successful teacher who stimulates research in his students.

Biffen's activity is not by any means to be measured by his published work. Two of his new wheats—"Little Joss," which owes its value to its immunity from rust, and "Yeoman," which combines high yield with first-class baking quality—are among the most popular wheats in the country, and together account for something like a third or even a half of the wheat crop of England.

The Hughes Medal is awarded to Prof. Owen Williams Richardson for his researches on the passage of electricity through gases and especially for those relating to the emission of electrons from hot bodies, a subject which he has made his own and christened *Thermionicities*. The subject is of great industrial as well as of scientific importance.

The Tidal Motion in the Irish Sea, its Currents and its Energy.

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The first part of this paper is devoted to the derivation of results from the Laplacian theory, connecting the tidal flow and the form of the free surface of a sea rotating with the earth, and small enough to be taken as flat. The work is carried to a first approximation only, the motion relative to the earth being considered small in magnitude and simply harmonic with respect to the time. The relations obtained have been applied numerically to the tides in the Irish Sea, chosen because of the comparatively large amount of data available, and the agreement between theory and observation seems to be satisfactory.

In the second portion of the paper, the hydro-dynamical equations are discussed to a further approximation, and the mean rates of flow of water and of transfer of energy across vertical sections are deduced, both depending on terms of the second order. These quantities are evaluated in the case of the Irish Sea, and two important results are obtained. It is shown that there is a steady residual drift of water northwards, of such a magnitude that the Sea would empty itself through the North Channel about once a year. The flow of energy into the Irish Sea through the two channels is also examined, and the total mean rate is found to be of the order 6×10^{17} ergs per second. This is approximately the same as the result obtained recently by Mr. G. I. Taylor,* working on the assumption of broken hydraulic flow, and confirmed, by calculation of the flow of energy, on the hypothesis of the current being a simple harmonic function of the time, and the same at all points in a vertical line.

The assumption of a purely harmonic flow clearly involves that the uncompensated part of the transfer of both water and energy must take

* G. I. Taylor, 'Phil. Trans.,' A, vol. 220, pp. 1-33 (1919). Calculations based on this latter assumption were made by the present writer in 1916 in connection with his previous paper ('Roy. Soc. Proc.,' A, vol. 93, pp. 348-359 (1917)), but were held up on account of the uncertainty of the effect both of the non-periodic terms in the current flow and also of the variation of this flow with the depth. The completion of the work has been prevented until the present time by teaching duties and military service.

place within a distance from the mean surface level equal to the amplitude in elevation of the tidal wave. On the other hand, the presence of a non-harmonic part in the flow may cause such transfer at all levels. It is shown that, in the case of the residual flow of water in the Irish Sea, the latter part is of importance in the result.

The total mean rate of flow of tidal energy into the Irish Sea thus determined is about 250 times the mean rate of dissipation of energy in the deeper portion of this region deduced by the author from a result involving surface velocities only, calculated on the tacit assumption of laminar motion throughout. The tidal energy is that of motion relative to the rotating earth, but it can easily be seen that this relative energy is independently conserved, although the total energy of the northward-moving stream of water varies with the latitude. Thus, any disappearance of the relative energy must take place *in situ* and, as Mr. Taylor contends, is to be ascribed mainly to local turbulent or eddying motion.

The Form of the Tidal Wave determines the Surface Currents.

As a first approximation, we regard a portion of the sea as a flat area rotating about a vertical axis, Oz , with the component angular velocity of diurnal motion, and suppose that the relative motion of the water is very small. Let the axes of x, y rotate in their plane with the prescribed angular velocity, ω , and let u, v be the components of the horizontal velocity, relative to these axes, of the particle of water which at time t is at (x, y, z) . The equations of motion are then*

$$\frac{\partial u}{\partial t} - 2\omega v = -g \frac{\partial \zeta}{\partial x}, \quad \frac{\partial v}{\partial t} + 2\omega u = -g \frac{\partial \zeta}{\partial y}, \quad (1)$$

where ζ is the elevation of the surface above its mean level.

For a simple harmonic wave we can write

$$\zeta = H \cos \sigma(t - T), \quad (2)$$

so that, from (1), u, v are each of the form $a \sin \sigma t + b \cos \sigma t$. The hodograph of the (u, v) motion is thus an ellipse, which actually is very elongated, and by taking the x -axis along its major axis we can write

$$u = W \cos \sigma(t - \tau), \quad v = w \sin \sigma(t - \tau). \quad (3)$$

In equations (2), (3), H, T, W, w, τ are functions of x, y ; W is the maximum, and w the minimum current velocity at the point, w/W being small numerically, T is the time of high water, and τ is the time of "flood-stream."

* See for example Lamb, 'Hydrodynamics,' § 206.

Substituting for ζ , u , v in (1) and remembering that the equations are true for all values of t we find

$$\left. \begin{aligned} gH_x &= (\sigma W + 2\omega w) \sin \sigma (T - \tau) \\ -gH_y &= (2\omega W + \sigma w) \cos \sigma (T - \tau) \\ g\sigma HT_x &= (\sigma W + 2\omega w) \cos \sigma (T - \tau) \\ g\sigma HT_y &= (2\omega W + \sigma w) \sin \sigma (T - \tau) \end{aligned} \right\}, \quad (4)$$

where the suffixes denote partial differentiations.

Now let $H' = \sqrt{(H_x^2 + H_y^2)}$, $T' = \sqrt{(T_x^2 + T_y^2)}$ so that H' , T' are the maximum surface up-gradients of H , T : also let χ be the angle between the directions of H' , T' , measured in this sense. Then from equations (4) we obtain the equations

$$(\sigma \pm 2\omega)(W \pm w) = g \sqrt{\{H'^2 \pm 2\sigma HH'T' \sin \chi + \sigma^2 H^2 T'^2\}}. \quad (5)$$

These equations are independent of the directions of the axes; and if H , T are known everywhere in the neighbourhood of a point, we can calculate from them W , w , so that *the magnitudes of the surface currents can be deduced from the lines of equal range of the tide and the co-tidal lines.*

The elimination of T from (4) gives

$$\left(\frac{gH_x}{\sigma W + 2\omega w}\right)^2 + \left(\frac{gH_y}{2\omega W + \sigma w}\right)^2 = 1, \quad (6)$$

from which w can be calculated if W and the gradients of H are known.

For the present problem the equation of continuity is

$$-\frac{\partial \zeta}{\partial t} = \frac{\partial (hu)}{\partial x} + \frac{\partial (hv)}{\partial y},$$

where h is the mean depth. Substituting from (2) and (3) for ζ , u , v , and neglecting the variation in h , this gives for a region in which τ is constant

$$\frac{\partial W}{\partial x} = -\frac{\sigma H}{h} \sin \sigma (T - \tau), \quad \frac{\partial w}{\partial y} = \frac{\sigma H}{h} \cos \sigma (T - \tau). \quad (7)$$

The Tides of the Irish Sea.

The main tidal wave from the Atlantic approaches the British Isles from a south-westerly direction, the crest being approximately at right angles to the direction of propagation. Ultimately it is divided into three distinct portions, which advance up the English Channel, the Irish Sea, and the west coasts of Ireland and Scotland. The two latter waves affect the motion within the Irish Sea, and their crests reach the St. George's Channel and the North Channel respectively almost simultaneously, namely, at 6 h. 25 m. G.M.T. on the days* of full and change of the moon. At this time it is low

* All the data used refer to these days.

water, or nearly so, on the Lancashire coast. The amplitude of the southern wave varies from about $4\frac{1}{2}$ feet on the Irish coast to $10\frac{1}{2}$ feet on the Welsh coast along the line at which it enters the Irish Sea, while that of the northern wave is about 2 feet when it enters the North Channel. The southern undulation dominates the motion as far as the south of Scotland.

The range of tide between high and low water is known with considerable accuracy along the coasts. Captain Beechey,* in his 'Report on the Tides of the Irish Sea,' gives a chart showing the lines of equal range over the whole area. These lines are almost equally spaced along any section drawn from the Irish to the Welsh coasts—a result which was *a priori* probable, and, as Mr. Taylor has shown,† can be inferred from simple dynamical reasoning.

In the same way, the time of high water, or establishment, is known accurately along the coast, but only approximately in other places. The chart of co-tidal lines used is that issued by the Admiralty. In the southern region of the Irish Sea the divergence between different charts of these lines is not very large, but near the North Channel some (or all) are quite unreliable.‡ For this reason these first order calculations have not been applied to places further north than the Calf of Man.

Captain Beechey's Report shows also the lines of the in-going or flood stream. The out-going stream does not differ materially from the reverse of this except that in the St. George's Channel it presses rather more towards the Irish coast.

Throughout the whole of the area the maximum surface current occurs at 8 h. 22 m., so that τ is a constant. The magnitudes of this current at certain points on a number of sections are given in the Admiralty publication, 'The Tides and Tidal Streams of the British Islands.'§ The following sections have been used for the present purpose:—

Section I. Tuskar Island ($52^{\circ} 12' N.$, $6^{\circ} 12' W.$) to St. David's Head ($51^{\circ} 54' N.$, $5^{\circ} 19' W.$).

Section II. Near the South End of Arklow Bank ($52^{\circ} 42' N.$, $6^{\circ} 0' W.$) to Bardsey Island ($52^{\circ} 45' N.$, $4^{\circ} 48' W.$).

Section III. Near Kish Lightship ($53^{\circ} 19\frac{1}{2}' N.$, $5^{\circ} 54' W.$) to North Stack, Holyhead ($53^{\circ} 19\frac{1}{2}' N.$, $4^{\circ} 41' W.$).

* 'Phil. Trans.,' p. 105 (1848). This report is the basis of the most recent Admiralty publications.

† *Loc. cit.*, ante, p. 9.

‡ The wave moves very slowly through the North Channel, its rate of progress being about two miles per hour, while further south its motion is very rapid, and the space gradients of T are quite indeterminable. The variation in longitude throughout the region has been neglected.

§ The greater part of the description of the tidal motion is derived from this source.

Section IV. Rockabill ($53^{\circ} 36' \text{ N.}, 6^{\circ} 0' \text{ W.}$) to the Calf of Man ($54^{\circ} 3' \text{ N.}, 4^{\circ} 50' \text{ W.}$).

Section V. The Calf of Man to Skerries Lighthouse ($53^{\circ} 25' \text{ N.}, 4^{\circ} 36' \text{ W.}$).

Each of these sections is divided into five approximately equal portions, and the maximum current at each of the points of division is recorded. These stations are denoted by Ia, Ib, ... IIa, ... the numeral denoting the section on which the station is situated.

In addition to the above, detailed hourly observations are available for the following lightships within this region:—(A) South Arklow ($52^{\circ} 41' \text{ N.}, 5^{\circ} 56' \text{ W.}$), (B) Cardigan Bay ($52^{\circ} 24' \text{ N.}, 5^{\circ} 0' \text{ W.}$), (C) North Arklow ($52^{\circ} 54' \text{ N.}, 5^{\circ} 50' \text{ W.}$), (D) Codling Bank ($53^{\circ} 4' \text{ N.}, 5^{\circ} 45' \text{ W.}$), (E) Carnarvon Bay ($53^{\circ} 6' \text{ N.}, 4^{\circ} 44' \text{ W.}$), (F) Kish ($53^{\circ} 19\frac{1}{2}' \text{ N.}, 5^{\circ} 54' \text{ W.}$). These stations are denoted by the letters A ... F.

The results of observations and of measurements made on the charts are shown in Table I. For convenience the units in common use are retained; heights are measured in feet, distances in nautical miles, and speeds in knots. A blank in a column indicates that the gradient is relatively small and uncertain. For the purpose of calculation its value is taken as zero.

Comparison of First-order Theory with Observations.

Equation (6) determines w when W, H_x, H_y are known, but the calculation is simplified if the first two equations (4) are used, $\sigma(T-\tau)$ being considered an unknown variable, θ . Writing for the semi-diurnal tide $\sigma = 2\Omega$ and $\omega = \Omega \sin \lambda$, where Ω is the earth's axial rotation and λ is the latitude, we have from (4)

$$\left. \begin{aligned} gH_x &= 2\Omega(W + w \sin \lambda) \sin \theta \\ -gH_y &= 2\Omega(W \sin \lambda + w) \cos \theta \end{aligned} \right\}, \quad (8)$$

from which by eliminating w

$$gW^{-1}(H_x \cos \theta + H_y \sin \lambda \sin \theta) = \Omega \cos^2 \lambda \sin 2\theta. \quad (9)$$

From this equation θ is found; either of the equations (8) then determines w .

As results are required at each of the observing stations a graphical solution is most convenient, and owing to the small variation of $\cos^2 \lambda$ over the southern part of the Irish Sea one graph of the function on the right of equation (9) is sufficient.

Table I.—Observational Data.

Station.	Feet.		Feet per nautical mile.		G.M.T.	Hours per nautical mile.	Degrees.	Knots.	
	H.	H'.	H _x .	H _y .	T.	T'.	χ.	W.	w.
Ia	5.0	0.14	-0.09	-0.12	h. m. 6 20	0.06	195	3	
Ib	5.8	0.13	-0.06	-0.12	6 50	0.04	165	2.8	
Ic	7.0	0.09	—	-0.09	6 5	0.04	30	2.5	
Id	7.5	0.16	—	-0.12	6 15	0.05	60	4	
A	1.8	0.23	0.16	-0.19	7 50	0.07	80	3.2	-0.3
B	6.5	0.06	—	-0.06	6 40	0.02	80	2.5	-0.4
IIa	2.8	0.17	0.10	-0.12	7 55	0.09	80	3.6	
IIb	4.3	0.16	0.08	-0.13	7 40	0.08	80	3.2	
IIc	6.0	0.14	0.06	-0.14	7 30	0.08	90	3.2	
IId	7.5	0.10	—	-0.10	7 35	0.09	90	3	
C	3.5	0.14	0.14	-0.07	8 50	0.14	85	3.8	0
D	5.0	0.14	0.12	-0.07	9 30	0.14	90	3.5	-0.3
E	7.9	0.08	—	—	8 55	0.07	0	2.2	0
F	6.5	0.10	0.06	-0.07	11 0	0.13	105	2.2	0
IIIa	7.0	0.10	0.08	-0.06	10 20	0.16	115	2	
IIIb	7.5	0.08	0.06	-0.05	9 30	0.06	105	2.5	
IIIc	8.3	0.07	0.05	-0.05	9 20	0.05	30	2.5	
IIId	9.0	0.08	0.06	-0.05	10 0	0.10	0	3.5	
IVa	7.5	0.08	0.04	0.07	11 20	?	140	1	
IVb	8.3	0.07	0.05	-0.05	11 0	0.16	110	0.5	
IVc	9.1	0.05	0.04	—	10 50	0.13	110	1.2	
IVd	9.6	0.11	0.06	—	11 0	0.07	135	1.2	
Va	10.3	0.10	0.09	—	10 50	0.06	250	2.5	
Vb	10.4	0.12	0.12	—	10 30	0.04	310	1.5	
Vc	10.3	0.14	0.14	—	10 15	0.03	340	2.0	
Vd	10.2	0.14	0.14	—	10 15	0.03	0	3.0	

With the units used, equation (9) becomes

$$W^{-1} \sqrt{(H_x^2 + 0.64 H_y^2)} \sin(\alpha - \theta) = 0.0084 \sin 2\theta, \quad (10)$$

where $H_x \operatorname{cosec} \alpha = -0.8 H_y \sec \alpha = \sqrt{(H_x^2 + 0.64 H_y^2)}$,

so that if it is assumed that $W + w \sin \lambda$ and $W \sin \lambda + w$ are both positive,* the angles α , θ , are in the same quadrant.

The second column of Table II gives the values of θ obtained by graphical solution of (10), and the third column the values of w deduced from (8). The results are of the right order of magnitude and with one exception† are numerically less than the corresponding values of W . The last column of Table I contains the values of w deduced from the hodographs of the observed

* W is positive, and usually w/W is of order less than $\frac{1}{2}$.

† For Station IVa. As might have been foreseen, the general agreement is closer in the south, where the tidal range is smaller.

Table II.

Station.	θ (degrees).	w (knots).	$W + w$ (knots).		
			Calculated.	Observed.	W (observed). w (calculated).
Ia	-33	0.7	2.2	—	3.7
Ib	-23	0.6	2.3	—	3.4
Ic	0	0.0	2.3	—	2.5
Id	0	-0.6	4.0	—	3.4
A	39	2.7	3.5	2.9	
B	0	-0.7	1.3	2.1	
IIa	34	0.2	3.7	—	3.8
IIb	28	1.0	4.0	—	4.2
IIc	20	0.6	4.6	—	3.8
IId	0	-0.3	5.2	—	2.7
C	59	-0.1	4.2	3.8	
D	52	-0.4	6.1	3.1	
E	?	?	3.7	2.2	
F	35	0.0	5.7	2.2	
IIIa	49	0.4	7.6	—	2.4
IIIb	41	-0.6	3.3	—	1.9
IIIc	32	-0.8	3.1	—	1.7
IIId	35	-1.5	5.7	—	2.0
IVa	-43	1.3	?	—	2.3
IVb	45	1.1	8.4	—	1.6
IVc	90	-0.5	7.9	—	0.7
IVd	90	0.2	5.2	—	1.4
Va	90	-0.5	2.7	—	2.0
Vb	90	1.5	1.7	—	3.0
Vc	90	1.4	1.0	—	3.4
Vd	90	0.2	2.5	—	3.2

velocities at the lightships A ... F, and except in one case the calculated results are in close agreement.

Since $\theta = \sigma(T - \tau)$ and $\tau = 8$ h. 22 m., the values of T can be deduced from those of θ . No great accuracy is possible, but the values of θ indicate (except in the case of IVa) the progress of the tidal wave northward.

With the same units as before (5) becomes

$$\left. \begin{aligned} W + w &= 12 \sqrt{(H'^2 + 1.1 HH'T' \sin \chi + 0.27 H^2 T'^2)} \\ W - w &= 110 \sqrt{(H'^2 - 1.1 HH'T' \sin \chi + 0.27 H^2 T'^2)} \end{aligned} \right\}, \quad (11)$$

but as the numerical value of the second term in the bracket is found to be almost equal to the sum of the other two terms, the second of these equations is quite useless. The fourth column of Table II gives the values of $W + w$ calculated from (11), and the following column such values of $W + w$ as can

be deduced directly from observations. For the stations on the five sections w is not known from observation, and its calculated value has been used. The values of $W + w$ so obtained are given in the last column.

The agreement between the observed and the calculated results is not so good as before. The variables here used for the first time depend entirely on the cotidal lines, so that the closeness of the agreement may be taken as a measure of their accuracy. It should, however, be mentioned that a glance at a chart will often suggest reasons for the more marked discrepancies due to the configuration of the coast or of the bed of the sea.

Integrating the first of equations (7) along a line of flood stream from A to B we obtain

$$W_A - W_B = \sigma \int_A^B \frac{H}{h} \sin \sigma(T - \tau) ds, \quad (12)$$

although no great accuracy is to be expected as the variation of h has been neglected previously.

The value of the integral can be found by graphical methods, the depths, h , being taken from a chart.* The ranges of integration are taken between the sectional lines I, II, III, V. The calculation has been carried out for the lines of flood-stream which cut Section I in the points ($52^\circ 5' \text{ N.}$, $5^\circ 54' \text{ W.}$) and ($52^\circ 2' \text{ N.}$, $5^\circ 45' \text{ W.}$). The Table shows the changes of W , as before measured in knots.

Range of integration.	First stream line.		Second stream line.	
	Calculated.	Observed.	Calculated.	Observed.
Section I to Section II	0.3	0.3	0.4	0.5
„ II „ III	0.0	-0.7	-0.1	-0.6
„ III „ V	-0.6	-1.0	-0.5	-0.5

Between Sections I and II and between Sections III and V the agreement is quite satisfactory. Between Sections II and III, the integrand changes from positive to negative, so that a small error in T will have an important effect on the integral, and very accurate results should not be expected.

From equation (7) it is seen that the value $T = \tau = 8 \text{ h. } 22 \text{ m.}$ makes W a maximum as far as variation with x is concerned. This result agrees well with observation.

The corresponding equation for the variation of w cannot usefully be evaluated in a similar manner as there are no sets of observed values of w with which to compare the results. Moreover, the change of h is much larger

* Admiralty Chart 1824A has been used.

here than in the previous case. It is, however, interesting to note that $\partial w / \partial y$ is positive in the southern portion of the Irish Sea, so that there should be a decrease in the value of w on crossing towards the Welsh coast in a direction at right angles to the lines of flood stream. Sections I, II, III, V are very nearly in this direction, and with two exceptions, the calculated values of w given in third column of Table II satisfy the required conditions.

A Second Approximation to Tidal Relations in a Flat Rotating Sea.

Using the same axes as before and taking the origin at the bottom of the sea, let the components of the relative velocities of the water referred to these axes be $U + U'$, $V + V'$, W' , where accented quantities are small compared with unaccented. Then if we retain terms of the two highest orders only the equations of motion may be written

$$\left. \begin{aligned} \frac{\partial}{\partial t} (U + U') + U \frac{\partial U}{\partial x} + V \frac{\partial U}{\partial y} - 2\omega (V + V') - \nu \Delta (U + U') \\ &= -\frac{\partial}{\partial x} (\Phi + \Phi') \\ \frac{\partial}{\partial t} (V + V') + U \frac{\partial V}{\partial x} + V \frac{\partial V}{\partial y} + 2\omega (U + U') - \nu \Delta (V + V') \\ &= -\frac{\partial}{\partial y} (\Phi + \Phi') \\ \frac{\partial W'}{\partial t} - \nu \Delta W' &= -\frac{\partial}{\partial z} (\Phi + \Phi') \end{aligned} \right\}, \quad (13)$$

where ν is the coefficient of viscosity and the space gradients of Φ' are small compared with those of Φ .

The first approximation to these equations is

$$\left. \begin{aligned} \frac{\partial U}{\partial t} - 2\omega V - \nu \frac{\partial^2 U}{\partial z^2} &= -\frac{\partial \Phi}{\partial x} \\ \frac{\partial V}{\partial t} + 2\omega U - \nu \frac{\partial^2 V}{\partial z^2} &= -\frac{\partial \Phi}{\partial y} \end{aligned} \right\}. \quad (14)$$

The solution in deep water represents motion vanishing at the bottom; in terms of complex velocities, $\mathbf{U}$, $\mathbf{V}$ it is given* by

$$\mathbf{U} \pm i\mathbf{V} = (\mathbf{U}_0 \pm i\mathbf{V}_0) \left[1 - \exp \left\{ -\frac{\alpha}{\beta} \right\} (1 + i)z \right], \quad (15)$$

where $\mathbf{U}_0$, $\mathbf{V}_0$ are the surface values of $\mathbf{U}$, $\mathbf{V}$, and $2\nu\alpha^2 = \sigma + 2\omega$, $2\nu\beta^2 = \sigma - 2\omega$, the motion being simple harmonic with the speed σ of

* R. O. Street, *loc. cit.*, *ante*. The rejection of the other terms depending on the viscosity is there justified. It is assumed that ω is not exceedingly small compared with σ and Ω .

the tide under consideration. In obtaining these results, we have replaced $\tanh \alpha h$ and $\tanh \beta h$ by unity; but, as $1/\alpha = 12$ cm. and $1/\beta = 25$ cm., the error so introduced is excessively small in deep water.

If we now assume that we can replace $\Delta(U', V')$ by $\partial^2(U', V')/\partial z^2$, the parts of (13) which are independent of the time are

$$\left. \begin{aligned} 2\omega v + \nu \frac{\partial^2 u}{\partial z^2} &= \frac{1}{2} \Sigma \left(U_r \frac{\partial}{\partial x} + V_r \frac{\partial}{\partial y} \right) U_r + \frac{\partial \phi}{\partial x} \\ -2\omega u + \nu \frac{\partial^2 v}{\partial z^2} &= \frac{1}{2} \Sigma \left(U_r \frac{\partial}{\partial x} + V_r \frac{\partial}{\partial y} \right) V_r + \frac{\partial \phi}{\partial y} \\ \nu \frac{\partial^2 w}{\partial z^2} &= \frac{\partial \phi}{\partial z} \end{aligned} \right\}, \quad (16)$$

where u, v, w, ϕ are the parts of U', V', W', Φ' , which are independent of the time, and we have written, as is clearly permissible from (14),

$$U = U_1 \cos \sigma t + U_2 \sin \sigma t, \quad V = V_1 \cos \sigma t + V_2 \sin \sigma t. \quad (17)$$

The summation refers to the values $r = 1, 2$.

From the last of equations (16)

$$\phi + f(x, y) = \nu \frac{\partial w}{\partial z} = -\nu \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right),$$

so that, to the degree of approximation already used, $\partial \phi / \partial x$ and $\partial \phi / \partial y$ are independent of z .

Now let the real parts of $\mathbf{U}_0, \mathbf{V}_0$, which we may call the components of the surface currents, be

$$p_1 \cos \sigma t + p_2 \sin \sigma t, \quad q_1 \cos \sigma t + q_2 \sin \sigma t. \quad (18)$$

Then from the first two of equations (16) after some reduction

$$\left(\nu \frac{\partial^2}{\partial z^2} - 2i\omega \right) (u + iv) = \left(\frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right) \phi + (S + iT) [P(S + iT) + Q(S - iT)], \quad (19)$$

where

$$\left. \begin{aligned} 2S &= 2 - e^{-\alpha z} \cos \alpha z - e^{-\beta z} \cos \beta z \\ 2T &= e^{-\alpha z} \sin \alpha z - e^{-\beta z} \sin \beta z \end{aligned} \right\}, \quad (20)$$

$$4 \left\{ \begin{matrix} P \\ Q \end{matrix} \right\} = \Sigma \left[(p_r \pm iq_r) \left(\frac{\partial}{\partial x} \mp i \frac{\partial}{\partial y} \right) (p_r + iq_r) \right] \quad r = 1, 2$$

so that P, Q , are independent of z .

The right-hand side of equation (19) is thus seen to take the form

$$P + Q + \left(\frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right) \phi + \Sigma (lP + mQ) e^{-(a\alpha + b\beta)z}$$

where the summation includes nine terms and a, b, l, m are numerical, the real parts of a, b being positive. Hence, if $\nu\gamma^2 = 2i\omega$, the solution of (19),

with the boundary conditions u, v zero at the bottom $z = 0$, $\partial(u, v)/\partial z$ zero at $z = h$, is given by

$$u + v = \frac{\iota}{2\omega} \left[P + Q + \frac{\partial\phi}{\partial x} + \iota \frac{\partial\phi}{\partial y} \right] \left[1 - \frac{\cosh \gamma(h-z)}{\cosh \gamma h} \right] + \Sigma \frac{(\iota P + mQ)[e^{-\delta z} \cosh \gamma h + \delta \gamma^{-1} e^{-\delta h} \sinh \gamma z - \cosh \gamma(h-z)]}{\nu(\delta^2 - \gamma^2) \cosh \gamma h}, \quad (21)$$

where $\delta = a\alpha + b\beta$ and δ^2 is not equal to γ^2 in any term.

For our future work we shall require to integrate u from 0 to h . Integrating (21), we find after some reduction as the first approximation,

$$\int_0^h (u + v) dz = \frac{\iota h}{2\omega} \left[P + Q + \frac{\partial\phi}{\partial x} + \iota \frac{\partial\phi}{\partial y} \right].$$

Taking now the axis of x parallel to the direction of the flood stream at the surface, we obtain from this

$$\int_0^h u dz = -\frac{h}{4\omega} \left(w \frac{\partial w}{\partial y} - 2 \frac{\partial\phi}{\partial y} \right), \quad (22)$$

where w now denotes the minimum surface velocity at (x, y) , as in equation (3).

The second equation in (16) applied to the bottom of the sea becomes

$$\left(\nu \frac{\partial^2 v}{\partial z^2} \right)_0 = \frac{\partial\phi}{\partial y},$$

so that near the bottom we have

$$v = Cz + \frac{z^2}{2\nu} \frac{\partial\phi}{\partial y}.$$

We may thus suppose that $\partial\phi/\partial y$, and so also $\nu \partial^2 v/\partial z^2$, is of the order $\nu w/h^2$, and therefore in deep water small compared with ωu . Hence with this special orientation of axes the second equation (16) at the surface takes the form

$$-2\omega u = \frac{1}{2} w \frac{\partial w}{\partial y}, \quad (23)$$

while (22) may be replaced by

$$\int_0^h u dz = -\frac{hw}{4\omega} \frac{\partial w}{\partial y}, \quad (24)$$

which, by (23) is equivalent to stating that the surface value of u is to this approximation equal to its mean value.

The Flow of Water across a Vertical Section.

Taking the section in the plane yOz , the rate at which water crosses per unit length is approximately

$$\int_0^{h+\zeta} U dz + \int_0^h U' dz.$$

If F is the mean value of this flow taken over a long period

$$F = \text{Mean value of } \int_{h-H}^{h+\zeta} U dz + \int_0^h u dz. \quad (25)$$

The first integral for a section normal to the direction of the flood stream at the surface becomes

$$\frac{1}{2} HW \cos \sigma (T - \tau), \quad (26)$$

which by equation (4) is equivalent to

$$-\frac{gH}{4\omega} \frac{\partial H}{\partial y}, \quad (27)$$

on the assumption that $\sigma w/2\omega W$ may be neglected.*

Using (24) in (25) we find

$$F = -\frac{1}{4\omega} \left(hw \frac{\partial w}{\partial y} + gH \frac{\partial H}{\partial y} \right). \quad (28)$$

The Transfer of Energy across a Vertical Section.

Taking the same section, the rate of transfer of energy per unit length is

$$\int_0^{h+\zeta} \{ g\rho(z-h) + \frac{1}{2}\rho Q^2 + \Pi \} Q_x dz, \quad (29)$$

where Q is the relative velocity of the water, Q_x its component along Ox , ρ the density of the water, supposed uniform, and Π the pressure. The mean level of the sea is taken as the zero of potential energy.

If l is the height of the water barometer at sea level, and

$$\Pi = g\rho(l+h+\zeta-z) + P',$$

so that P' is relatively small, (29) can to our approximation be replaced by

$$g\rho(l+\zeta) \int_0^{h+\zeta} U dz + \int_0^h \{ g\rho l U' + \frac{1}{2}\rho U(U^2 + V^2) + U P' \} dz.$$

The mean value of the first integral is†

$$\frac{1}{2} g\rho(h+l) HW \cos \sigma (T - \tau),$$

* This transformation is made to eliminate T , and thereby to make possible the subsequent numerical work. The error introduced is probably less than that arising from the uncertainty as to the values of T .

† Neglecting l , this is equivalent to the expression given by Mr. G. I. Taylor (*loc. cit. ante*), for the total rate of transfer of energy.

which (on the same assumption as before) can be replaced by

$$\frac{-g^2\rho(h+l)H}{4\omega}\frac{\partial H}{\partial y}.$$

The mean value of the second integral is to our approximation

$$g\rho l \int_0^h u dz.$$

Thus if K_0 denotes the mean rate of transfer of energy per unit length of section

$$K_0 = \frac{-g\rho}{4\omega} \left\{ lhw \frac{\partial w}{\partial y} + g(h+l)H \frac{\partial H}{\partial y} \right\}. \quad (30)$$

If the zero of potential energy were taken at a height k above mean sea-level ($z-h$) in (29) would be replaced by ($z+k-h$), and in place of (30) we should have

$$K_k = \frac{-g\rho}{4\omega} \left\{ (l-k)hw \frac{\partial w}{\partial y} + g(l+h-k)H \frac{\partial H}{\partial y} \right\}, \quad (31)$$

so that from (28)

$$K_0 - K_k = g\rho kF.$$

If any two sections of the type considered are taken right across any channel, the integrals of F along them must be the same in the absence of any permanent change in the volume of water.* Hence in estimating the total transfer of energy into the region between them it is immaterial what zero of potential energy is used, provided the same is used for both. This is evident from physical considerations; it assumes that both mean sea-levels are on the same gravitational equipotential surface. Equation (31) takes its simplest form when $k=l$, when it may be written

$$K = \frac{-g^2\rho hH}{4\omega} \frac{\partial H}{\partial y}. \quad (32)$$

Numerical Evaluation of the Transfer of Energy.

Sufficient data exist to enable the integrals to be evaluated across certain sections of the Irish Sea.

Section I.—The deviation of the maximum surface current from the normal to the section nowhere exceeds six degrees and may be neglected. The direction of integration† is towards the Irish Coast, and $\partial H/\partial y$ is almost constant.

* It is easy to show that the change due to rainfall is negligible in the case of the Irish Sea.

† This is determined by the direction of the flood stream. Actually, the integrals are taken between the twenty-fathom lines, which are usually within a mile of the coast.

To evaluate the integral, the section is divided into four equal parts and the mean of the five values of hH obtained by Simpson's rule. For the five points we have

$$\begin{aligned} h &= 20, 49, 53, 51, 20 \text{ fathoms,} \\ H &= 8.4, 7.1, 6.3, 5.4, 4.5 \text{ feet,} \end{aligned}$$

so that the mean of hH is 285. Taking $\rho = 1.03$ we obtain from (32) for the mean northward transfer of energy

$$8.1 \times 10^{17} \text{ ergs per second.} \quad (33)$$

In a similar manner for Sections II and III we find

$$8.2 \times 10^{17} \text{ and } 6.4 \times 10^{17} \text{ ergs per second.} \quad (34), (35)$$

Section V is in a suitable direction and along it the total change in H does not exceed 6 inches, its values at the two ends being approximately equal. Since the values of hH are only slightly greater than on the previous sections, it follows that the value of the integral is relatively very small for this section, and to our order may be taken as zero.

For Section XII, Burrow Head ($54^\circ 41' \text{ N.}, 4^\circ 24' \text{ W.}$) to Ayre Point ($54^\circ 25' \text{ N.}, 4^\circ 22' \text{ W.}$). The mean rate of transfer is

$$0.2 \times 10^{17} \text{ ergs per second,} \quad (36)$$

the direction being eastward.

For Section VIII, Muck Island ($54^\circ 51' \text{ N.}, 5^\circ 43' \text{ W.}$) to Corsewall Point ($55^\circ 1' \text{ N.}, 5^\circ 9' \text{ W.}$) it is northward and of amount

$$1.1 \times 10^{17} \text{ ergs per second,} \quad (37)$$

while for Section VII, Tor Point ($55^\circ 12' \text{ N.}, 6^\circ 4' \text{ W.}$) to the Mull of Cantyre ($55^\circ 18' \text{ N.}, 5^\circ 48' \text{ W.}$), it is in a north-westerly direction and does not exceed

$$0.3 \times 10^{17} \text{ ergs per second.} \quad (38)$$

The Transfer of Water.

The term in the expression (28) for F which depends on w prevents any very exact calculations, but estimates can be made using the calculated values of w given in Table II. For each of the Sections I, II, III a result in the neighbourhood of 10^{11} c.c. per second is obtained, the contributions from the two terms of the integral being of the same order of magnitude.* Sufficient information is not available to obtain reliable results for integrations across the North Channel.

* To check the results, the first term in the expression for F has been evaluated directly from (26) without making use of (4), T being obtained from the chart of cotidal lines. For the three sections, the results $0.4, 0.8, 0.9 \times 10^{11}$ c.c. per sec. were obtained.

Discussion of the Results.

The estimation of the transfer of energy is somewhat arbitrary, owing to the absence of any precise zero of potential energy. The integrals evaluated on the hypothesis that the zero level is at a height above mean sea level equal to the height of the water barometer are, from (35)—(38):

For the southern sections $8.1, 8.2, 6.4 \times 10^{17}$ C.G.S. units

For the northern sections $1.1, 0.3 \times 10^{17}$ C.G.S. units,

the last being a maximum result. In each case the mean transfer is northward.

Now, throughout the Irish Sea the mean sea level is not constant, there being a rise of about 2 feet from the south to the north.* A further correction must be introduced since Ordnance levels are not of gravitational equipotential surfaces. We shall probably be safe if we suppose that, referred to an equipotential surface, the variation of mean sea level in the Irish Sea does not exceed a metre, and in this limit we may include any correction due to variation of mean atmospheric pressure. Thus the *maximum* corrections to be applied to any of the integrals to refer it to the same level as that used for Section VII is 100 *gpF*, or, say, 10^{16} ergs per second. As this certainly falls within the limit of error, it may be ignored.

Subtracting the integrals for the extreme Sections I and VII, we find, as the mean rate of transfer of energy into the Irish Sea,

$$7.8 \times 10^{17} \text{ ergs per second.}$$

Actually, this result must be too large, for both the current velocities and the tidal ranges have been taken at their spring-tide values. At neap tides *H* is reduced to about three-quarters of this value, and presumably the currents will be decreased in about the same ratio.† Hence, as we are dealing with products, it is probably a good approximation to say that the mean rate of transfer of energy into the Irish Sea is‡

$$6 \times 10^{17} \text{ ergs per second.}$$

A detailed examination of the integrals shows that about one-third of this energy is gained by the portion of the sea south of a line drawn west through Holyhead, while only a small fraction of it flows into the region east of a line through the Isle of Man.

* See G. B. Airey, 'Phil. Trans.,' 1845, p. 1. I am indebted to the Ordnance Survey for this reference.

† The introduction of long periods is of course inconsistent with the hypothesis that *H, w* are independent of the time.

‡ Mr. Taylor's estimate (correcting a slight error in his working) is 7.2×10^{17} ergs per second.

The residual flow of water is of the order 10^{11} c.c. per second, or 3000 cubic kilom. per annum, allowing for the reduction due to the long period motion. As the total water-content of the Irish Sea is about 3000 cubic kilom., we can say that it empties itself about once a year through the North Channel.

This residual drift of water has been evaluated previously by M. Knudsen* as equal at least to a yearly emptying of the Irish Sea. Its actual existence has been demonstrated by Dr. Bassett† and others from observations of the temperature and the salinity of the water at different periods of the year. Assuming the drift to be spread uniformly over the whole section, the residual velocity would be about 2 cm. per second, or 1 mile per day, in St. George's Channel, and about twice as much in the narrowest part of the North Channel.

My thanks are due to Sir Joseph Larmor for much valuable criticism of this paper before its communication to the Society.

[*Note added, December 8.*—The question has been suggested by a referee how far the horizontal forces causing this residual drift might be compensated by a small permanent slope of the free surface. But the motion has been estimated from the actual observed surface levels, so that the effect in thus partially piling up the water is discounted. The obstruction of the North Channel shows that this piling effect must be considerable; it is only if the northern exit were wholly obstructed that all horizontal forces would be compensated by the change of level.]

* "Some Remarks on the Currents in the North Sea and Adjacent Waters," 'Pubs. de Circonstance,' vol. 39 (Conseil Perm. Internat. pour l'Exploration de la Mer).

† 'Liverpool Biol. Soc. Trans.,' vol. 24, p. 148 (1910); see also vol. 17, p. 154 (1903).

Electrification of an Insulated Lens, treated by the Stream-force-function; and Allied Problems.

By Sir G. GREENHILL, F.R.S.

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The chief object of this memoir was the calculation of the Stokes' stream-current or force-function, S , representing uniaxial surfaces having meridian section of a line of force, orthogonal to the uniaxial potential function, V , with special reference to the electrical problems discussed by Prof. H. M. Macdonald in the 'Proceedings of the London Mathematical Society' (L.M.S.), vol. 26, 1895, in a body bounded by spherical surfaces, as a lens.

1. The expression for V , the potential function (P.F.) of a lens, insulated and electrified to potential π , has been given by Macdonald in the form

$$V_0 - V = \pi - V = C - D, \quad (1)$$

where, changing his η and ξ into u and v ,

$$C = \int_u^\infty \frac{\sqrt{(\text{ch } u - \cos v)}}{\sqrt{(\text{ch } \xi - \text{ch } u)}} \frac{\text{sh } f\xi \cdot f d\xi}{\text{ch } f\xi - \cos f v}, \quad (2)$$

$$D = \int \frac{\sqrt{(\text{ch } u - \cos v)}}{\sqrt{(\text{ch } \xi - \text{ch } u)}} \frac{\text{sh } f\xi \cdot f d\xi}{\text{ch } f\xi - \cos f(v + 2\beta)}, \quad (3)$$

so that C is derived from D by putting $\beta = 0$, or else D is derived from C by replacing $f v$ by $f(v + 2\beta)$.

Here, in the figure, u and v are the stereographic dipolar co-ordinates, connected with the Cartesian x and y by the conformal relation

$$y + ix = a \coth \frac{1}{2}(u + iv), \quad \text{or} \quad x + iy = a \cot \frac{1}{2}(v + iu), \quad (4)$$

$$x, y = a \frac{\sin v, \text{sh } u}{\text{ch } u - \cos v}, \quad (5)$$

and u is constant along a parallel of latitude on the stereographic projection of the hemisphere, with A and B as South and North Pole, while v is constant along a meridian, as on the figure.

In C and D of (2) and (3), $v = \alpha - \beta$ and $v = -\beta$ over the two boundary spherical surfaces of the lens, and $\alpha = \pi/f$ is the salient angle of the dielectric space outside the lens, the dielectric angle.

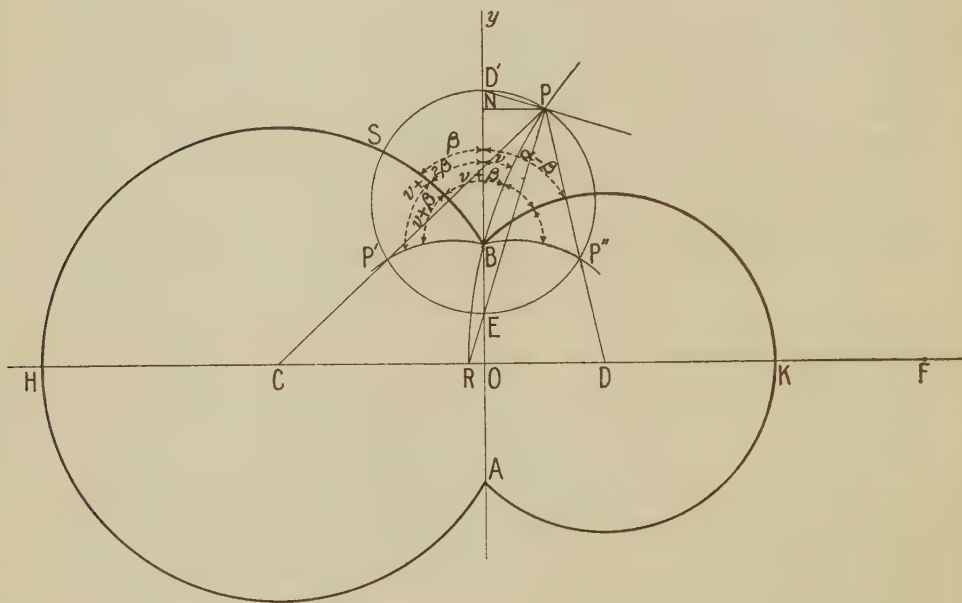
With C on the figure the centre of the circle $v = -\beta$,

$$CA = a \text{ cosec } \beta, \quad CP^2 = (x + a \cot \beta)^2 + y^2 = \frac{\text{ch } u - \cos(u + 2\beta)}{\text{ch } u - \cos v} CA^2, \quad (6)$$

$$D = \frac{CA}{CP} \cdot E, \text{ where } E = \int \sqrt{\left[\frac{\text{ch } u - \cos(v+2\beta)}{\text{ch } \xi - \text{ch } u} \right] \frac{\text{sh } f\xi \cdot f d\xi}{\text{ch } f\xi - \cos f(v+2\beta)}}, \quad (7)$$

so that E is derived from C in (2) by a change of v throughout into $v+2\beta$.

Then since $f\alpha = \pi$, $\cos f(v+2\beta) = \cos f v$, $C = D$, $V = \pi$, over both the spherical surfaces of the lens, $v = \alpha - \beta$ and $v = -\beta$.



The circle ABP through P is defined by v , and thus $-v-2\beta$ defines the circle ABP' through the inverse point, P', in the sphere $v = -\beta$; and at the pole B, the circular arcs BP, BP' make equal angles with the spherical surface $v = -\beta$.

2. We have to verify that V satisfies Laplace's equation. In these orthogonal conjugate function co-ordinates, u and v , Laplace's equation becomes

$$\frac{d}{du} \left(y \frac{dV}{du} \right) + \frac{d}{dv} \left(y \frac{dV}{dv} \right) = 0,$$

$$\text{or} \quad \frac{d}{du} \left(\frac{\text{sh } u}{\text{ch } u - \cos v} \cdot \frac{dV}{du} \right) + \frac{d}{dv} \left(\frac{\text{sh } u}{\text{ch } u - \cos v} \cdot \frac{dV}{dv} \right) = 0. \quad (A)$$

Here the differentiation of V, C, D in § 1 with respect to v does not introduce any difficulty. But with respect to u , there is the extra term to be considered due to the lower limit u , and this term is infinite, and will require to be cancelled by some other infinity under the integration.

We have then to write

$$C = \int_u^\infty C_1 d\xi, \quad \frac{dC}{du} = \int_u^\infty \left(\frac{dC_1}{du} + \frac{dC_1}{d\xi} \right) d\xi, \quad (1)$$

and trust to the cancelling of the infinities between $\frac{dC_1}{d\xi}$ and $\frac{dC_1}{du}$.

In Hicks's manner for his toroidal function, putting

$$C = P \sqrt{(\text{ch } u - \cos v)}, \quad P = \int \frac{d\xi}{\sqrt{(\text{ch } \xi - \text{ch } u)}} \cdot \frac{f \text{ sh } f \xi}{\text{ch } f \xi - \cos f v}, \quad (2)$$

Laplace's equation (A) then changes into

$$\frac{d^2 P}{du^2} + \coth u \frac{dP}{du} + \frac{d^2 P}{dv^2} + \frac{1}{4} P = 0, \quad \text{or} \quad \frac{d}{d\mu} (\mu^2 - 1) \frac{dP}{d\mu} + \frac{d^2 P}{dv^2} + \frac{1}{4} P = 0, \quad (3)$$

with $\text{ch } u = \mu$, and the differentiations are simplified thereby.

In another conformal representation similar to (4), § 1,

$$z + iw = f \coth \frac{1}{2} f (\zeta + iv), \quad z = \frac{f \text{ sh } f \zeta}{\text{ch } f \zeta - \cos f v}, \quad (4)$$

$$C_1 = \sqrt{\left(\frac{\text{ch } u - \cos v}{\text{ch } \xi - \text{ch } u} \right)} z, \quad P_1 = \frac{z}{\sqrt{(\text{ch } \xi - \text{ch } u)}}, \quad P = \int_u^\infty P_1 d\xi, \quad (5)$$

and we have to cancel the infinity arising at the lower limit u , making use of the differentiations

$$\begin{aligned} \frac{dP}{du} &= \int \left(d \frac{P_1}{d\xi} + \frac{dP_1}{du} \right) d\xi \\ &= \int \frac{d\xi}{\sqrt{(\text{ch } \xi - \text{ch } u)}} \left[\frac{dz}{d\xi} - \frac{1}{2} z \coth \frac{1}{2} (\xi + u) \right], \end{aligned} \quad (6)$$

$$\frac{d^2 P}{du^2} = \int \frac{d\xi}{\sqrt{(\text{ch } \xi - \text{ch } u)}} \left[\frac{d^2 z}{d\xi^2} - \frac{dz}{d\xi} \coth \frac{1}{2} (\xi + u) + \frac{1}{2} z \text{ cosec}^2 \frac{1}{2} (\xi + u) + \frac{1}{4} z \right], \quad (7)$$

and then

$$\frac{d^2 P}{du^2} + \coth u \frac{dP}{du} + \frac{1}{4} P = \int \frac{N d\xi}{\sqrt{(\text{ch } \xi - \text{ch } u)}}, \quad (8)$$

$$N = \frac{d^2 z}{d\xi^2} + \frac{dz}{d\xi} \frac{\text{sh } \frac{1}{2} (\xi - u)}{\text{sh } u \text{ sh } \frac{1}{2} (\xi + u)} + \frac{1}{4} z \frac{-\text{sh } \xi + 2 \text{ sh } u}{\text{sh } u \text{ sh}^2 \frac{1}{2} (\xi + u)}, \quad (9)$$

$$\frac{N}{\sqrt{(\text{ch } \xi - \text{ch } u)}} = \frac{1}{\sqrt{(\text{ch } \xi - \text{ch } u)}} \cdot \frac{d^2 z}{d\xi^2} + \frac{d}{d\xi} \frac{\frac{1}{2} z [\text{sh } \frac{1}{2} (\xi - u)]^{1/2}}{\text{sh } u [\text{sh } \frac{1}{2} (\xi + u)]^{3/2}}, \quad (10)$$

$$\frac{d^2 P}{du^2} + \coth u \frac{dP}{du} + \frac{1}{4} P = \int \frac{d\xi}{\sqrt{(\text{ch } \xi - \text{ch } u)}} \cdot \frac{d^2 z}{d\xi^2} + * \quad (11)$$

the star * denoting an integral which vanishes at both limits of ξ , u and ∞ .

These precautions are not required in the differentiation with respect to v , so that Laplace's equation becomes

$$\int \frac{d\zeta}{\sqrt{(\text{ch } \zeta - \text{ch } u)}} \left(\frac{d^2 z}{d\zeta^2} + \frac{d^2 z}{dv^2} \right) = 0, \quad (12)$$

and so it is satisfied by P, and also by C, and the same procedure will serve for D.

3. Our chief object in this memoir is to discover S, the orthogonal stream-force function (S.F. or F.F.) of the P.F.V; a surface $S = \text{a constant}$ containing the lines of force in a meridian section.

Laplace's equation in (A), §2, is equivalent to

$$\frac{dS}{du} = +y \frac{dV}{dv}, \quad \frac{dS}{dv} = -y \frac{dV}{du}, \quad (1)$$

omitting Maxwell's factor 2π ; and then

$$\frac{dV}{dv} = \frac{1}{y} \frac{dS}{du}, \quad \frac{dV}{du} = -\frac{1}{y} \frac{dS}{dv}, \quad (2)$$

so that Laplace's equivalent equation for the S.F. is

$$\frac{d}{du} \left(\frac{1}{y} \frac{dS}{du} \right) + \frac{d}{dv} \left(\frac{1}{y} \frac{dS}{dv} \right) = 0. \quad (B)$$

With the stereographic co-ordinates of §1, we have to put

$$S = \frac{R}{\sqrt{(\text{ch } u - \cos v)}}, \quad (3)$$

to obtain the equation (B) in the form

$$\frac{d^2 R}{du^2} - \coth u \frac{dR}{du} + \frac{d^2 R}{dv^2} + \frac{1}{4} R = 0, \quad \text{or} \quad (\mu^2 - 1) \frac{d^2 R}{d\mu^2} + \frac{d^2 R}{dv^2} + \frac{1}{4} R = 0. \quad (4)$$

We may take for correspondence

$$S = \int z \sqrt{\left(\frac{\text{ch } \zeta - \text{ch } u}{\text{ch } u - \cos v} \right)} d\zeta, \quad R = \int z \sqrt{(\text{ch } \zeta - \text{ch } u)} d\zeta, \quad (5)$$

$$\frac{dR}{du} = \int \left[\frac{dz}{d\zeta} + \frac{1}{2} z \coth \frac{1}{2} (\zeta + u) \right] \sqrt{(\text{ch } \zeta - \text{ch } u)} d\zeta, \quad (6)$$

$$\frac{d^2 R}{du^2} = \int \left[\frac{d^2 z}{d\zeta^2} + \frac{dz}{d\zeta} \coth \frac{1}{2} (\zeta + u) - \frac{1}{2} z \text{cosec} \frac{1}{2} (\zeta + u) + \frac{1}{4} z \right] \sqrt{(\text{ch } \zeta - \text{ch } u)} d\zeta, \quad (7)$$

$$\begin{aligned} \frac{d^2 R}{du^2} - \coth u \frac{dR}{du} + \frac{1}{4} R &= \int \left\{ \frac{d^2 z}{d\zeta^2} \sqrt{(\text{ch } \zeta - \text{ch } u)} + \frac{d}{d\zeta} \frac{[\frac{1}{2} z \text{sh } \frac{1}{2} (\zeta - u)]^{3/2}}{\text{sh } u [\text{sh } \frac{1}{2} (\zeta + u)]^{1/2}} \right\} d\zeta \\ &= \int \frac{d^2 z}{d\zeta^2} \sqrt{(\text{ch } \zeta - \text{ch } u)} d\zeta + * \quad (8) \end{aligned}$$

so that (4) is satisfied provided z is any conjugate function of ζ and v in (4), §2.

4. Corresponding to the separate terms in V, C, and D, in § 1, we take

$$S = a(A - B), \quad (1)$$

satisfying the separate conditions

$$\frac{dA}{du} = -\frac{y}{a} \frac{dC}{dv}, \quad \frac{dA}{dv} = +\frac{y}{a} \frac{dC}{du}, \quad (2)$$

$$\frac{dB}{du} = -\frac{y}{a} \frac{dD}{dv}, \quad \frac{dB}{dv} = +\frac{y}{a} \frac{dD}{du}, \quad (3)$$

and then

$$\frac{dS}{adu} = \frac{dA}{du} - \frac{dB}{du} = -\frac{y}{a} \frac{dC}{dv} + \frac{y}{a} \frac{dD}{dv} = +\frac{y}{a} \frac{dV}{dv}, \quad (4)$$

$$\frac{dS}{adv} = -\frac{y}{a} \frac{dV}{du}. \quad (5)$$

There does not appear to be any direct method of writing down the integrals required for A, B, S. But by various conjectural considerations we are led to infer that we may take A, the S.F. of the P.F.C. of the form

$$A = \int_u^\infty A_1 f d\zeta, \quad (6)$$

$$A_1 = \sqrt{\left(\frac{\text{ch } \zeta - \text{ch } u}{\text{ch } u - \cos v}\right) \frac{\sin v}{\text{ch } \zeta - \cos v} \cdot \frac{\text{sh } f\zeta}{\text{ch } f\zeta - \cos fv}} \\ - \sqrt{\left(\frac{\text{ch } u - \cos v}{\text{ch } \zeta - \text{ch } u}\right) \frac{\text{sh } \zeta}{\text{ch } \zeta - \cos v} \cdot \frac{\sin fv}{\text{ch } f\zeta - \cos fv}}, \quad (7)$$

and derive B, the S.F. of D, by writing $f(v + 2\beta)$ for fv ;

$$B_1 = \sqrt{\left(\frac{\text{ch } \zeta - \text{ch } u}{\text{ch } u - \cos v}\right) \frac{\sin v}{\text{ch } \zeta - \cos v} \cdot \frac{\text{sh } f\zeta}{\text{ch } f\zeta - \cos f(v + 2\beta)}} \\ - \sqrt{\left(\frac{\text{ch } u - \cos v}{\text{ch } \zeta - \text{ch } u}\right) \frac{\text{sh } \zeta}{\text{ch } \zeta - \cos v} \cdot \frac{\sin f(v + 2\beta)}{\text{ch } f\zeta - \cos f(v + 2\beta)}}. \quad (8)$$

We have to verify then that

$$\frac{a}{y} \frac{dA}{du} + \frac{dC}{dv} = 0, \quad \frac{a}{y} \frac{dA}{dv} - \frac{dC}{du} = 0, \quad \frac{y}{a} = \frac{\text{sh } u}{\text{ch } u - \cos v}. \quad (9)$$

Performing the differentiation, we find

$$\frac{\text{ch } u - \cos v}{\text{sh } u} \frac{dA_1}{du} + \frac{dC_1}{dv} = \frac{d}{d\zeta} \sqrt{\left(\frac{\text{ch } u - \cos v}{\text{ch } \zeta - \text{ch } u}\right) \frac{\sin fv}{\text{ch } f\zeta - \cos fv}}, \quad (10)$$

and here an infinity arises at the lower limit u , to be cancelled by writing

$$\frac{\text{ch } u - \cos v}{\text{sh } u} \left(\frac{dA_1}{d\zeta} + \frac{dA_1}{du} \right) + \frac{dC_1}{dv} \\ = \frac{d}{d\zeta} \frac{\sqrt{(\text{ch } u - \cos v \cdot \text{ch } \zeta - \text{ch } u)}}{\text{sh } u} \cdot \frac{\sin v}{\text{ch } \zeta - \cos v} \cdot \frac{\text{sh } f\zeta}{\text{ch } f\zeta - \cos fv} \\ + \frac{d}{d\zeta} \sqrt{\left(\frac{\text{ch } u - \cos v}{\text{ch } \zeta - \text{ch } u}\right) \left(1 - \frac{\text{sh } \zeta}{\text{sh } u} \cdot \frac{\text{ch } u - \cos v}{\text{ch } \zeta - \cos v}\right) \frac{\sin fv}{\text{ch } f\zeta - \cos fv}}, \quad (11)$$

in which the second line reduces to

$$\frac{d}{d\xi} \sqrt{\frac{(\operatorname{ch} u - \cos v \cdot \operatorname{ch} \xi - \operatorname{ch} u)}{\operatorname{sh} u}} \cdot \frac{\operatorname{ch} \frac{1}{2}(\xi - u) - \operatorname{ch} \frac{1}{2}(\xi + u) \cos v}{\operatorname{sh} \frac{1}{2}(\xi + u)(\operatorname{ch} \xi - \cos v)} \cdot \frac{\sin fv}{\operatorname{ch} f\xi - \cos fv}, \quad (12)$$

so that, integrating with respect to ξ ,

$$\frac{\operatorname{ch} u - \cos v}{\operatorname{sh} u} \cdot \frac{dA}{du} + \frac{dC}{du} = * + * = 0, \quad (13)$$

provided $f > \frac{1}{2}$, $\alpha < 2\pi$ as required in a physical problem.

Proceeding in the same way with the other differentiations, we find

$$\begin{aligned} & \frac{\operatorname{ch} u - \cos v}{\operatorname{sh} u} \cdot \frac{dA_1}{dv} - \frac{dC_1}{d\xi} - \frac{dC_1}{du} \\ &= \frac{d}{d\xi} \sqrt{\left(\frac{\operatorname{ch} u - \cos v}{\operatorname{ch} \xi - \operatorname{ch} u} \right) \left(\frac{\operatorname{sh} \xi}{\operatorname{sh} u} \cdot \frac{\operatorname{ch} u - \cos v}{\operatorname{ch} \xi - \cos v} - 1 \right)} \frac{\operatorname{sh} f\xi}{\operatorname{ch} f\xi - \cos fv} \\ &= \frac{d}{d\xi} \sqrt{\frac{(\operatorname{ch} u - \cos v \cdot \operatorname{ch} \xi - \operatorname{ch} u)}{\operatorname{sh} u}} \cdot \frac{\operatorname{ch} \frac{1}{2}(\xi + u) \cos v - \operatorname{ch} \frac{1}{2}(\xi - u)}{\operatorname{sh} \frac{1}{2}(\xi + u)(\operatorname{ch} \xi - \cos v)} \\ & \quad \cdot \frac{\operatorname{sh} f\xi}{\operatorname{ch} f\xi - \cos fv}, \quad (14) \end{aligned}$$

and integrating with respect to ξ ,

$$\frac{\operatorname{ch} u - \cos v}{\operatorname{sh} u} \frac{dA}{dv} - \frac{dC}{du} = * = 0, \quad (15)$$

so that the conditions in (9) are both satisfied.

Similarly for B and D.

5. To verify our conjectures concerning A and B, we test the preceding formulas on a few of the simplest cases.

Begin with the complete sphere, for which $f = 1$, and the dielectric angle is two right angles, $\alpha = 180^\circ$. Then in (2) § 1,

$$C = \pi, \quad E = \pi, \quad V = \pi \frac{CA}{CP}. \quad (1)$$

In the S.F., $A = 0$; and with $\operatorname{ch} \xi = s$, $\operatorname{ch} u = b$,

$$\begin{aligned} B &= \int_b^\infty \sqrt{\left(\frac{s-b}{b-\cos v} \right) \frac{\sin v ds}{s-\cos v \cdot s-\cos(v+2\beta)}} \\ & \quad - \int \sqrt{\left(\frac{b-\cos v}{s-b} \right) \frac{\sin(v+2\beta) ds}{s-\cos v \cdot s-\cos(v+2\beta)}} \\ &= - \int \sqrt{\left(\frac{b-\cos v}{s-b} \right) \frac{\cot \beta ds}{s-\cos v}} \\ & \quad + \frac{\operatorname{ch} u \cos \beta - \cos(v+\beta)}{\sin \beta \sqrt{(b-\cos v)}} \int \frac{ds}{\sqrt{(s-b)}} \cdot \frac{1}{s-\cos(v+2\beta)}. \quad (2) \end{aligned}$$

Making use of the lemmas of the Integral Calculus

$$\int_b^\infty \frac{ds}{\sqrt{(s-b)}} \cdot \frac{1}{s-c} = \frac{\pi}{\sqrt{(b-c)}}, \quad \text{and} \quad \int \frac{ds}{\sqrt{(s-b)}} \cdot \frac{1}{(s-c)^2} = \frac{\frac{1}{2}\pi}{(b-c)^{3/2}}, \quad (3)$$

by a differentiation with respect to c ,

$$\begin{aligned} B &= -\pi \cot \beta + \frac{\pi}{\sin \beta} \cdot \frac{\text{ch } u \cos \beta - \cos(v+\beta)}{\sqrt{[\text{ch } u - \cos v \cdot \text{ch } u - \cos(v+2\beta)]}} \\ &= -\pi \cot \beta + \frac{CA}{OA} \cos \text{OCP}, \quad (4) \end{aligned}$$

$$S = \alpha(A-B) = \pi \cdot OA - \pi \cdot CA \cos \text{OCP}, \quad (5)$$

of which the constant term may be ignored.

6. Next for two orthogonal spherical surfaces, as shown in the figure, with centres at C and D; $f=2$, and the dielectric angle is a right angle, $\alpha=90^\circ$.

With $\text{ch } \zeta = s$, here

$$\begin{aligned} D &= \int \sqrt{\left(\frac{\text{ch } u - \cos v}{s - \text{ch } u}\right)} \frac{2s ds}{s^2 - \cos^2(v+2\beta)} \\ &= \int \sqrt{\left(\frac{\text{ch } u - \cos v}{s - \text{ch } u}\right)} \left[\frac{ds}{s - \cos(v+2\beta)} + \frac{ds}{s + \cos(v+2\beta)} \right] \\ &= \pi \sqrt{\frac{\text{ch } u - \cos v}{\text{ch } u - \cos(v+2\beta)}} + \pi \sqrt{\frac{\text{ch } u - \cos v}{\text{ch } u + \cos(v+2\beta)}} \\ &= \pi \frac{CA}{CP} + \pi \frac{DA}{DP}; \quad (1) \end{aligned}$$

and putting $\beta=0$,

$$C = \pi + \pi \sqrt{\frac{\text{ch } u - \cos v}{\text{ch } u + \cos v}} = \pi + \pi \frac{OA}{OP}, \quad (2)$$

$$\frac{V}{\pi} = 1 - \frac{C-D}{\pi} = +\frac{CA}{CP} + \frac{DA}{DP} - \frac{OA}{OP}, \quad (3)$$

the potential of the three electric images at C, D, O.

Over the surface AHB, centre C, and D, O inverse points in this sphere, $\frac{OA}{OP} = \frac{DA}{DP}$, while $CA = CP$, $V = \pi$; and over AKB, centre D, and C, O inverse points, $\frac{OA}{OP} = \frac{CA}{CP}$, $DA = DP$, $V = \pi$.

For the S.F., with $\text{ch } u = b$, $\cos v = c$,

$$\begin{aligned}
 A &= \int \sqrt{\left(\frac{s-b}{b-c}\right) \frac{\sin v}{s-c}} \cdot \frac{4s ds}{2(s^2-c^2)} - \int \sqrt{\frac{b-c}{s-b} \frac{\sin 2v}{s-c}} \cdot \frac{2ds}{2(s^2-c^2)} \\
 &= \frac{2\sin v}{\sqrt{(b-c)}} \int \frac{ds}{\sqrt{(s-b)}} \cdot \frac{s^2-bs-bc+c^2}{(s-c)^2(s+c)} \\
 &= \frac{2\sin v}{\sqrt{(b-c)}} \int \frac{ds}{\sqrt{(s-b)}} \left[-\frac{a-c}{(s-c)^2} + \frac{\frac{1}{2}}{s-c} + \frac{\frac{1}{2}}{s+c} \right] \\
 &= \frac{2\sin v}{\sqrt{(b-c)}} \left[-\frac{\frac{1}{2}\pi(a-c)}{(a-c)^{3/2}} + \frac{\frac{1}{2}\pi}{\sqrt{(a-c)}} + \frac{\frac{1}{2}\pi}{\sqrt{(a+c)}} \right] \\
 &= \frac{\pi \sin v}{\sqrt{(b^2-c^2)}} = \frac{\pi \sin v}{\text{ch } u - \cos v} \cdot \sqrt{\frac{\text{ch } u - \cos v}{\text{ch } u + \cos v}} = \frac{\pi x}{\text{OP}} = \pi \cos x \text{OP}. \quad (4)
 \end{aligned}$$

And then for B, with $\cos(v+2\beta) = c'$,

$$\begin{aligned}
 B &= \int \sqrt{\left(\frac{s-b}{b-c}\right) \frac{\sin v}{s-c}} \frac{4s ds}{2(s^2-c'^2)} - \int \sqrt{\left(\frac{b-c}{s-b}\right) \frac{\sin(v+2\beta)}{s-c}} \cdot \frac{4c' ds}{2(s^2-c'^2)}, \\
 &\quad (5) \\
 aB &= -2\pi a \cot 2\beta + \pi \cdot \text{CA} \cdot \cos \text{OCP} + \pi \cdot \text{DA} \cdot \cos \text{ODP}, \quad (6)
 \end{aligned}$$

by the reductions as above and ignoring the constant term $2\pi a \cot 2\beta$,

$$S = a(A-B) = \pi \cdot \text{OA} \cos x \text{OP} - \pi \cdot \text{CA} \cdot \cos \text{OCP} - \pi \cdot \text{DA} \cos \text{ODP}, \quad (7)$$

and here the three terms represent the S.F. of the three images at O, C, D, with capacity represented by the radius OA, CA, DA.

Generally, for f an integer, as in L.M.S., vol. 26, p. 167, the P.F. and S.F. of the lens is due to a series of f images, arranged along the line of centres.

7. Next for a spherical bowl, AHB in the figure; with $f = \frac{1}{2}$, and dielectric angle, $\alpha = 360^\circ$. Then, with $\text{ch } \frac{1}{2}\zeta = s$,

$$\begin{aligned}
 C &= \int_u^\infty \sqrt{\left(\frac{\text{ch } u - \cos v}{\text{ch } \zeta - \text{ch } u}\right) \frac{\text{sh } \frac{1}{2}\zeta \cdot \frac{1}{2}d\zeta}{\text{ch } \frac{1}{2}\zeta - \cos \frac{1}{2}v}} = \int \sqrt{\left(\frac{\text{ch}^2 \frac{1}{2}u - \cos^2 \frac{1}{2}v}{s - \text{ch}^2 \frac{1}{2}u}\right) \frac{ds}{s - \cos \frac{1}{2}v}} \\
 &= \sin^{-1} \sqrt{\left(\frac{\text{ch } u - \cos v}{\text{ch } u + 1}\right) \frac{\sqrt{(s^2 - \text{ch}^2 \frac{1}{2}u)}}{s - \cos \frac{1}{2}v}} \Bigg|_u^\infty \\
 &= \sin^{-1} \sqrt{\frac{\text{ch } u - \cos v}{\text{ch } u + 1}} = \sin^{-1} \frac{\text{AB}}{\text{AP} + \text{PB}} = \omega, \quad (1)
 \end{aligned}$$

the P.F. of the circular disc on AB, when electrified to potential $\frac{1}{2}\pi$.

Similarly, writing $\text{ch } \frac{1}{2}u = b$, $\cos \frac{1}{2}(v+2\beta) = c'$,

$$\begin{aligned}
 E &= \int \sqrt{\left(\frac{b^2 - c'^2}{s^2 - b^2}\right) \frac{ds}{s - c'}} = \sin^{-1} \sqrt{\left(\frac{b^2 - c'^2}{b^2}\right) \frac{\sqrt{(s^2 - b^2)}}{s - c'}} \Bigg|_b^\infty \\
 &= \sin^{-1} \sqrt{\left(1 - \frac{c'^2}{b^2}\right)} = \cos^{-1} \frac{c'}{b} = \omega', \quad (2)
 \end{aligned}$$

suppose, and $D = \frac{\text{CA}}{\text{CP}} \omega'$.

But if P' is the point inverse to P in the spherical surface AHB , $v = -\beta$,

$$\begin{aligned} \frac{AB}{AP' + P'B} &= \frac{AB}{(CA/CP) \cdot AP + (CB/CP) PB} = \frac{CP}{CA} \sin \omega \\ &= \sqrt{\frac{\text{ch } u - \cos(v + 2\beta) \cdot \text{ch } u - \cos v}{\text{ch } u - \cos v \cdot \text{ch } u + 1}} = \sqrt{\frac{\text{ch } u - \cos(v + 2\beta)}{\text{ch } u + 1}} \\ &= \sqrt{\frac{b^2 - c'^2}{b^2}} = \sin \omega', \quad (3) \end{aligned}$$

and ω' is the P.F. at P' of the electrified disc on AB .

When the bowl is electrified to potential π , this makes

$$V = \pi - \omega + \frac{CA}{CP} \omega', \quad (4)$$

instead of the usual form given, due to taking a different starting point for the multiple values of ω and ω' .

Draw the co-axial circle through P, P' , crossing the sphere of the bowl at S, S' ; and let P, P' circulate round this circle in opposite directions.

Starting with P and P' in coincidence at S on the bowl, where $CP = CP' = CA$, the multiplicity is chosen so as to make $\omega = \omega'$ at S , $V = \pi$. Then P, P' proceed in opposite directions, and cross again at S' , where $CP = CP' = CA$, but $\omega' = \pi - \omega$; thus over the blank zone AKB of the spherical surface, $V = 2\omega'$, double of the P.F. of the electrified disc AB , and this is not constant.

This verifies when the bowl is a complete sphere, and $AB = 0$. For if P is an internal point, $\omega = \omega' = 0$, $V = \pi$; but, if P is external, $\omega = \omega' = \pi$, $V = \pi \frac{CA}{CP}$.

Proceeding with the S.F. for $f = \frac{1}{2}$, and first for A , from (7), § 4, with $\cos \frac{1}{2}v = e$,

$$\begin{aligned} A &= \int \sqrt{\left(\frac{s^2 - b^2}{b^2 - e^2}\right)} \cdot \frac{\sin v ds}{2(s^2 - e^2)(s - e)} - \int \sqrt{\left(\frac{b^2 - e^2}{s^2 - b^2}\right)} \frac{\sin \frac{1}{2}v \cdot 2s ds}{2(s^2 - e^2)(s - e)} \\ &= \frac{\sin \frac{1}{2}v}{\sqrt{(b^2 - e^2)}} \int \frac{ds}{\sqrt{(s^2 - b^2)}} \cdot \frac{es - b^2}{(s - e)^2} \\ &= \frac{\sin \frac{1}{2}v}{\sqrt{(b^2 - e^2)}} \left[-\frac{\sqrt{(s^2 - b^2)}}{s - e} \right]_b^\infty = -\frac{\sin \frac{1}{2}v}{\sqrt{(b^2 - e^2)}} = -\sqrt{\frac{1 - \cos v}{\text{ch } u - \cos v}} \\ &= -\sqrt{\left(1 - \frac{\text{ch } u - 1}{\text{ch } u - \cos v}\right)} = -\sqrt{\left[1 - \left(\frac{r_1 - r_2}{2a}\right)^2\right]}, \quad (6) \end{aligned}$$

so that $-Aa$ is the semi-conjugate axis of the hyperbola through P , foci at A, B .

Next, from (8), § 4, for B, with $\cos \frac{1}{2}(v+2\beta) = c$,

$$B = \int \sqrt{\frac{(s^2-b^2)}{(b^2-e^2)}} \frac{\sin v \, ds}{2(s^2-e^2)(s-c)} - \int \sqrt{\frac{(b^2-e^2)}{(s^2-b^2)}} \frac{\sin \frac{1}{2}(v+2\beta) \cdot 2s \, ds}{2(s^2-e^2)(s-b)} \\ = \frac{1}{\sqrt{(b^2-e^2)}} \int \frac{ds}{\sqrt{(s^2-a^2)}} \left(\frac{L_1}{s-e} + \frac{L_2}{s+e} + \frac{L_3}{s-b} \right), \quad (7)$$

and, working out the partial fractions and integration, we find, after reduction,

$$Ba = CA (\omega' \cos PCO - \omega), \quad (8)$$

the S.F. of D, agreeing with the result obtained by J. R. Wilton in the 'Messenger of Mathematics,' August, 1914.

8. In the geometry of the electrical inversion of the bowl with respect to a point, Q, on the rim, to obtain the electrification induced in a semi-infinite plate by a point charge at Q, I have to thank the kind assistance of Mr. C. N. H. Lock, Fellow of Caius College.

The plane through a point, P, and the axis OC of the bowl, is shown in the figure, where the bisector, PR, of the angle APB crosses AB in E, and the axis OC in R, on the circle round APB, centre F.

The triangles EAP, BRP are similar, because $EAP = BRP$, $EPA = BPR$; and then

$$\sin \omega = \frac{AB}{AP+PB} = \frac{AE}{AP} = \frac{EB}{PB} = \frac{BR}{PR}. \quad (1)$$

Next invert with respect to any point, Q, on the circular edge, ABQ, of the bowl, with $QO_1 = AB$, the diameter the base, as the radius of inversion.

The circle QAB inverts into the edge O_1z of the semi-infinite plate, and in the plane of the figure through Q and the axis OC of the bowl, O_1x perpendicular to QC is the trace of the plate xO_1z , inverse of the bowl.

The circle, centre O_1 and radius O_1Q , is the inverse of the axis OC; and if R_1 is the inverse point of R, O_1R_1 is the trace of the plane $R_1O_1P_1$, inverse of the sphere through P, centre F; and P_1 being the inverse point of P,

$$\frac{QP_1}{P_1R_1} = \frac{QR}{PR} = \frac{BR}{PR} = \frac{AE}{AP} = \sin \omega. \quad (2)$$

This proves almost all that is required. Because, in electrical inversion, if ω is a P.F. at P, then

$$QP \cdot \omega = \frac{QO_1^2}{QP_1} \omega = \frac{AB^2}{QP_1} \sin^{-1} \frac{QP_1}{P_1R_1}, \quad (3)$$

is a P.F. at P_1 .

For the second part, $\frac{CA}{CP} \omega'$, in the P.F. of the bowl, draw the figure in the plane QPP'C, passing through QC, and so at right angles to the plate.

Then $CP \cdot CP' = CQ^2$, so that the circle round PQP' touches CQ at Q , and with P_1, P_1' , the inverse points of P, P' , inverted from Q , a circle goes round $PP'P_1'P_1$, and then $QP_1P_1' = QPP' = P'QC$, so that P_1P_1' is parallel to CQ , and so at right angles to the plate.

With Q' , the inverse point of the centre C of the bowl, optical image of Q in the plate,

$$\frac{Q'P_1'}{CP'} = \frac{QQ'}{QP'}, \text{ while } \frac{CP'}{QP'} = \frac{QC}{QP}, \quad (4)$$

because P, P' are inverse points in the bowl; thence

$$Q'P_1' = \frac{QQ' \cdot CP'}{QP'} = \frac{QQ' \cdot QC}{QP} = \frac{QO_1^2}{QP} = QP_1, \quad (5)$$

so that P_1P_1' is bisected at right angles by the plate; and P_1, P_1' are thus optical images in the plate, a general theorem.

Then with $\frac{CP'}{CA} \omega'$, a P.F. at P , a P.F. at the inverse point P_1 is

$$\frac{QP \cdot CP'}{CQ} \cdot \omega' = QP' \cdot \omega' = \frac{AB^2}{QP_1'} \sin^{-1} \frac{QP_1'}{P_1'R_1'} = \frac{AB^2}{Q'P_1} \sin^{-1} \frac{Q'P_1}{R_1P_1}; \quad (6)$$

because $QP_1' = Q'P_1, P_1'R_1' = R_1P_1$.

And since $PEER = DEEO = P'E.ER'$, a circle goes round $PRR'P'$; and $CR.CR' = CA^2$, so that R_1, R_1' are optical images in the plate.

The circle RBP through P is defined by v , and then $-v-2\beta$ defines the circle $R'BP'$ through P' ; thus, at the point B on the rim, the circular arcs BP, BP' make equal angles with the bowl BS , the curvilinear angles at B , PBS and SBP' , being equal. And AK bisects RAR' , where R, R' are inverse points in the bowl.

Then in the inversion, the planes $O_1R_1z, O_1R_1'z$ make equal angles with OC_1 , trace of the plane inverse of the bowl; and since R_1, R_1' lie on the circle, centre O_1 , and radius O_1Q_1 , they are optical images in this plane.

We infer from the inversion that

$$V_1 = \frac{1}{P_1Q} \sin^{-1} \frac{P_1Q}{P_1R_1} - \frac{1}{P_1Q'} \sin^{-1} \frac{P_1Q'}{P_1R_1'}, \quad (7)$$

is a potential function, zero over the semi-infinite plate, and so is the P.F. of the electrification induced by a point charge at Q .

To obtain this result from the form given by Macdonald in L.M.S., vol. 26, p. 163, replace on p. 162 his

$$\begin{aligned} & 2 \tan^{-1} \sqrt{\frac{\operatorname{ch} \frac{1}{2} \eta - \cos \frac{1}{2} (\theta - \theta')}{\operatorname{ch} \frac{1}{2} \eta + \cos \frac{1}{2} (\theta - \theta')}} \quad \text{by} \quad \cos^{-1} \frac{\cos \frac{1}{2} (\theta - \theta')}{\operatorname{ch} \frac{1}{2} \eta} \\ \text{or} \quad & \cos^{-1} \sqrt{\frac{1 + \cos (\theta - \theta')}{\operatorname{ch} \eta + 1}} = \sin^{-1} \sqrt{\frac{\operatorname{ch} \eta - \cos (\theta - \theta')}{\operatorname{ch} \eta + 1}}, \end{aligned} \quad (8)$$

and then, from p. 161,

$$2rr' \operatorname{ch} \eta = r^2 + r'^2 + z^2, \quad (9)$$

$$2rr' (\operatorname{ch} \eta + 1) = (r + r')^2 + z^2 = P_1 R_1^2, \quad (10)$$

$$2rr' [\operatorname{ch} \eta - \cos (\theta - \theta')] = Q P_1^2, \quad (11)$$

thus leading to the form above in (2), § 1, and to Sommerfeld's result.

The generalisation is obvious to Macdonald's result on p. 162, where $f = m + \frac{1}{2}$, half an odd integer; then for a point charge at Q in the dielectric space between two conducting planes to earth, at an angle $\frac{\pi}{f} = \frac{2\pi}{2m+1}$, the $4m+2$ optical images, Q_k , must be taken, including Q at Q_1 ; and the potential V_1 at P_1 of the induced electrification is given by

$$\frac{\pi V_1}{q} = \sum_{k=0}^{k=2m} \frac{(-1)^k}{P_1 Q_k} \sin^{-1} \frac{P_1 Q_k}{P_1 R_1}. \quad (12)$$

Inversion with respect to Q will give a lens again with dielectric angle $\frac{2\pi}{2m+1}$; and when electrified to potential π , the potential V at an external point P in the dielectric space will be given in the form

$$V = \pi - \sum (-1)^k \frac{CA}{CP_k} \omega_k, \quad (13)$$

where ω_k is the P.F. at P_k of the disc on AB, electrified to potential $\frac{1}{2}\pi$, $\omega_k = \sin^{-1} \frac{AB}{AP_k + P_k B}$.

9. The expression for the capacity, K, of a lens employed by Macdonald can be utilised as a verification of our expressions for the S.F., S.; this should give the same value to K, by the difference of the values of S, S_1 , and S_2 at H and K, vertex on the axis of the lens, in the form

$$K = \frac{S_1 - S_2}{2\pi}. \quad (1)$$

At H, $u = 0$, $v = -\beta$, $v + 2\beta = \beta$,

$$S_1 = 2a \sin f \beta \sqrt{(1 - \cos \beta)} \int \frac{\sqrt{(\operatorname{ch} \xi + 1)} f d\xi}{(\operatorname{ch} \xi - \cos \beta)(\operatorname{ch} f \xi - \cos f \beta)}, \quad (2)$$

and similarly at K, where $u = 0$, $v = \alpha - \beta$, $v + 2\beta = \alpha + \beta$,

$$S_2 = 2a \sin f \beta \sqrt{[1 - \cos (\alpha - \beta)]} \int \frac{\sqrt{(\operatorname{ch} \xi + 1)} f d\xi}{[\operatorname{ch} \xi - \cos (\alpha - \beta)](\operatorname{ch} f \xi + \cos f \beta)}. \quad (3)$$

Tested for the complete sphere, with $f = 1$, $\alpha = 180^\circ$,

$$S_1 = 2a \sin \beta \sqrt{1 - \cos \beta} \int \frac{\sqrt{(\operatorname{ch} \xi + 1) d\xi}}{(\operatorname{ch} \xi - \cos \beta)^2}$$

$$= 2a \sin \beta \sqrt{1 - \cos \beta} \int_1^\infty \frac{ds}{\sqrt{(s-1)(s-\cos \beta)^2}} = \frac{\pi a \sin \beta}{1 - \cos \beta}, \quad (4)$$

$$S_2 = \frac{-\pi a}{1 + \cos \beta}, \quad S_1 - S_2 = \frac{2\pi a}{\sin \beta} = 2\pi \cdot CA, \quad (5)$$

and the capacity K is the radius, CA .

For two orthogonal surfaces, $f = 2$, $\alpha = 90^\circ$,

$$S_1 = 2a \sin 2\beta \sqrt{1 - \cos \beta} \int \frac{\sqrt{(\operatorname{ch} \xi + 1) 2d\xi}}{(\operatorname{ch} \xi - \cos \beta)(\operatorname{ch} 2\xi - \cos 2\beta)}$$

$$= 4a \sin 2\beta \sin \frac{1}{2}\beta \int \frac{ds}{\sqrt{(s-1)} \cdot \frac{1}{(s-\cos \beta)^2(s+\cos \beta)}}$$

$$= \pi a (\operatorname{cosec} \beta + \cot \beta - \tan \beta + \sec \beta - 1), \quad (6)$$

$$S_2 = -\pi a (\sec \beta + \tan \beta - \cot \beta + \operatorname{cosec} \beta - 1), \quad (7)$$

$$K = \frac{S_1 - S_2}{2\pi} = a (\operatorname{cosec} \beta + \sec \beta - 1) = CA + DA - OA. \quad (8)$$

For the bowl, $f = \frac{1}{2}$, $\alpha = 360^\circ$, and with $\operatorname{ch} \frac{1}{2}\xi = s$, $\cos \frac{1}{2}\nu = c$,

$$S_1 = 2a(1 - c^2) \int \frac{ds}{\sqrt{(s^2 - 1)}} \cdot \frac{s}{(s - c)^2(s + c)}, \quad (9)$$

$$S_2 = -2a(1 - c^2) \int \frac{ds}{\sqrt{(s^2 - 1)}} \cdot \frac{s}{(s - c)(s + c)^2}, \quad (10)$$

$$S_1 - S_2 = 4a(1 - c^2) \int_1^\infty \frac{ds}{\sqrt{(s^2 - 1)}} \cdot \frac{s^2}{(s^2 - c^2)^2}, \quad (11)$$

$$K = \frac{S_1 - S_2}{2\pi} = \frac{a}{2\pi} \cdot \frac{\pi - \beta + \sin(\pi - \beta)}{\sin \beta}$$

$$= \frac{\text{arc AHB} + \text{chord AOB}}{2\pi} = \frac{\text{girth}}{2\pi}, \quad (12)$$

as on the figure, and this verifies for the complete sphere, and the disc.

10. Encouraged by the verifications of our conjecture, for $f = 1, 2, \frac{1}{2}$, we proceed to test the S.F. method on the lens with conducting angle 90° , $\alpha = \frac{3}{2}\pi$, $f = \frac{2}{3}$; and for the hemisphere take $\beta = -\pi$, $\alpha - \beta = \frac{1}{2}\pi$.

As before, with $\operatorname{ch} \frac{1}{3}\xi = s$, $\cos \frac{1}{3}\beta = \cos \gamma = b$, $1 - \cos \beta = (1 - b)(1 + 2b)^2$
 $b_1 = \cos(\gamma + \frac{2}{3}\pi)$, $b_2 = \cos(\gamma + \frac{4}{3}\pi)$, $b_3 = \cos(\gamma + \pi) = -b$,

$$S_1 = \frac{1}{2}a \sqrt{1 - \cos 3\gamma} \sin 2\gamma \int \frac{ds}{\sqrt{(s-1)}} \cdot \frac{2s-1}{(s-b)^2(s-b_1)(s-b_2)(s-b_3)}, \quad (1)$$

and changing γ into $\frac{1}{2}\pi - \gamma$, with

$$c = \sin \gamma, c_1 = \sin(\gamma + \frac{2}{3}\pi), c_2 = \sin(\gamma + \frac{4}{3}\pi), c_3 = \sin(\gamma + \pi) = -c, \\ S_2 = -\frac{1}{2}a\sqrt{(1 + \sin 3\gamma) \sin 2\gamma} \int \frac{ds}{\sqrt{(s-1)}} \cdot \frac{2s-1}{(s-c)^2(s-c_1)(s-c_2)(s-c_3)}. \quad (2)$$

For S_1 , the resolution is required into the partial fractions of

$$\frac{2s-1}{(s-b)^2(s-b_1)(s-b_2)(s-b_3)} = \frac{L_1}{(s-b)^2} + \frac{L_2}{s-b} + \frac{L_3}{s-b_1} + \frac{L_4}{s-b_2} + \frac{L_5}{s-b_3}, \quad (3)$$

with $b = \cos \gamma$ replaced by $c = \sin \gamma$ for S_2 .

The work was heavy and the details are omitted here, but the verification with Macdonald's result was effected.

But it is advisable to put on record the values of L , or rather of the corresponding integrals of the partial fractions, as it did not prove an easy matter to get them right; so making use of the lemma

$$1 - \cos 3\gamma = (1 + 2b)^2(1-b) = (1 + 2b_1)^2(1-b_1) = \dots, \quad (4)$$

$$\frac{S_1}{\pi} = N_1 + N_2 + N_3 + N_4 + N_5, \quad (5)$$

$$N_1 = \frac{1 + \cos \gamma}{6 \sin \gamma}, \quad (6)$$

$$N_2 = -\frac{\sin \gamma}{6 \cos \gamma} + \frac{1 - \cos 2\gamma}{3 \sin 3\gamma}, \quad (7)$$

$$N_3 + N_4 = \frac{2 \sin 2\gamma}{\sqrt{3} \sin 6\gamma} - \frac{2}{3\sqrt{3}}, \quad N_5 = -\frac{1}{2 \cos 3\gamma} + \frac{1}{2}, \quad (8)$$

And similarly, in $-S_2$, with γ replaced by $\frac{1}{2}\pi - \gamma$,

$$M_1 = \frac{1 + \sin \gamma}{\cos \gamma}, \quad M_2 = -\frac{\cos \gamma}{6 \sin \gamma} + \frac{1 + \cos 2\gamma}{-3 \cos 3\gamma}, \\ M_3 + M_4 = \frac{2 \sin 2\gamma}{\sqrt{3} \sin 6\gamma} - \frac{2}{3\sqrt{3}}, \quad M_5 = -\frac{1}{-2 \sin 3\gamma} + \frac{1}{2}, \quad (9)$$

leading to the same value as before of

$$\frac{K}{a} = \frac{S_1 - S_2}{2\pi}. \quad (10)$$

Thus for the symmetrical lens, as before,

$$\beta = \frac{3}{4}\pi, \quad \gamma = \frac{1}{4}\pi, \quad N_1 = \frac{\sqrt{2+1}}{6}, \quad N_2 = -\frac{1}{6} + \frac{\sqrt{2}}{3}, \quad N_3 + N_4 = -\frac{2}{\sqrt{3}} - \frac{2}{3\sqrt{3}}, \\ N_5 = \frac{1}{\sqrt{2}} + \frac{1}{2}, \quad S_1 = -S_2; \quad \frac{K}{a} = 1 + 2\sqrt{2} - \frac{16}{3\sqrt{3}} = 0.7492.$$

But the indeterminate form arises in the flat hemispherical lens; and here $b = \frac{1}{2}$, so that a factor cancels, and L_1, N_1 , are absent.

11. The elliptic integral arises in the calculation of the P.F. and S.F. of the lens with $f = \frac{2}{3}, \frac{3}{4}$, and conducting angle $90^\circ, 120^\circ$.

With $f = \frac{2}{3}$, and $\text{ch } \frac{1}{3}\zeta = s$, $\text{ch } \frac{1}{3}u = b$, $\cos \frac{1}{3}v = c$,

$$\text{ch } \zeta - \text{ch } u = 4s^3 - 3s - 4b^3 + 3b = S,$$

$$\text{ch } u - \cos v = -S(c) = -S(-c) = 4b^3 - 3b - 4c^3 + 3c = -\Sigma,$$

$$C = \int_b^\infty \frac{\sqrt{-\Sigma}}{\sqrt{S}} \cdot \frac{2s ds}{s^2 - c^2} = \int \frac{\sqrt{-\Sigma}}{s - c} \cdot \frac{ds}{\sqrt{S}} + \int \frac{\sqrt{-\Sigma}}{s + c} \cdot \frac{ds}{\sqrt{S}}, \quad (1)$$

two complete elliptic integrals of the third kind in a standard form of Weierstrass; and here

$$g_2 = 3, \quad g_3 = \text{ch } u, \quad \Delta = -27 \text{sh}^2 u, \quad J = -\text{cosech}^2 u, \quad J - 1 = -\text{coth}^2 u. \quad (2)$$

So too with $f = \frac{3}{4}$, and $\text{ch } \frac{1}{4}\zeta = s$, $\cos \frac{1}{4}v = c$,

$$\cos(\frac{1}{4}v + \frac{2}{3}\pi) = c_1, \quad \cos(\frac{1}{4}v + \frac{4}{3}\pi) = c_2,$$

$$C = \int \sqrt{-\Sigma} \left(\frac{1}{s - c} + \frac{1}{s - c_1} + \frac{1}{s - c_2} \right) \frac{ds}{\sqrt{S}}. \quad (3)$$

The reduction of these integrals to a final result depending on tabulated functions is an interesting application of Elliptic Function theory.

The gravitation P.F. and S.F. of a homogeneous lens have been worked out in the 'American Journal of Mathematics,' vols. 33 and 39.

On the Proximity of Atoms in Gaseous Molecules.

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1. In a recent note* I have called attention to the degree of correspondence between W. L. Bragg's† estimates (based on X-ray crystal measurements) of the dimensions of certain atoms, and those deduced by means of the kinetic theory of gases from determinations of viscosity. I was not then fully aware of the modern work of Chapman‡ in relation to the latter subject, and made calculations by means of a formula which has been definitely superseded. The result was that the comparison gave only qualitative agreement. A closer examination of the data, in the light of Chapman's results, together with a new aspect of the matter which forms the main subject of the present paper, reveals certain interesting facts regarding the probable arrangement of atoms in molecules, and, in addition, leads to substantial *quantitative* agreement with Bragg's values.

2. From the very close agreement between the values of the atomic radius calculated by means of Chapman's formula,§ and from van der Waal's law, there appears now to be no room for doubt that, in the case of monatomic gases, at any rate, the atoms, when in thermal agitation, behave like hard spheres which exert mutual attraction on one another. It is also evident that the *absolute* diameters of these spheres are now known with considerable accuracy, sufficient to justify quoting to three significant figures. They are given for four monatomic gases in column 3 of Table I for comparison with Bragg's values, which appear in column 2. They differ to a slight extent from those calculated by Chapman himself, owing to the adoption in the present calculation of Millikan's|| recent value 2.705×10^{19} for the number of molecules per cubic centimetre at N.T.P. This differs by about 2 per cent. from that used by Chapman, and the substitution results in an increase of about 1 per cent. in the estimated atomic diameter.¶

* A. O. Rankine, 'Phil. Mag.,' vol. 40, p. 516 (October, 1920).

† W. L. Bragg, 'Phil. Mag.,' vol. 40, p. 169.

‡ S. Chapman, 'Phil. Trans.,' A, vol. 216, p. 279.

§ *Loc. cit.*, p. 347.

|| R. A. Millikan, 'Phil. Mag.,' vol. 34, p. 1.

¶ It may be pointed out that the formula obtained by Chapman upon the basis above-mentioned leads to values of the molecular dimensions which are independent of temperature. In this respect, among others, it is superior to those derived from

Table I.

Gas.	Atomic diameter.		Ratio (d/σ) = K.
	From crystal measurements, $2d$ (cm. $\times 10^{-8}$).	From viscosity measurements, 2σ (cm. $\times 10^{-8}$).	
Neon.....	1·30	2·35	0·553
Argon.....	2·05	2·87	0·714
Krypton.....	2·35	3·19	0·737
Xenon.....	2·70	3·51	0·769

W. L. Bragg regards his values as measures of the diameters of the outer electron shells of the respective atoms, and it will be seen that, from this point of view, the moving atoms of a gas do not approach so closely during an encounter that even the outer electrons intermingle. The atom, in so far as collision is concerned, is to be regarded as a hard elastic sphere of radius (σ) quite definitely greater than the distance (d) between the centre of the atom and its outer electrons. The ratios in column 4 show that the relation between these two radii is not one of strict proportionality, but depends on the particular type of atom.

3. When we come to consider the case of diatomic molecules—as, for example, in chlorine gas—we are met with the difficulty that we are no longer entitled to regard the molecule as a sphere. Hitherto, it has been customary to regard it as such, and obtain, by the formula which is strictly applicable to single atoms only, an average atomic diameter. In this paper an attempt is made to take into account the well-recognised fact that diatomic molecules are not completely symmetrical. Chapman's viscosity formula, in common with all previous ones, gives a means of calculating, not the atomic radius (σ) directly, but the quantity $\pi\sigma^2$, which is the area presented as a target by the atom to other atoms approaching from all possible directions. The author suggests that in applying the formula to molecules consisting of two atoms, while the calculation of the value of σ has no definite meaning, it is still possible to obtain a quantity equivalent to $\pi\sigma^2$, which will now represent the mean area which the molecule presents as a target for all possible orientations. We are not, however, justified in going further unless we know the actual shape of the molecule. It happens that the Lewis-Langmuir theory of atomic and

earlier theories in which the molecules were regarded as free from mutual attractions. The dimensions used in this paper are derived from Chapman's formula, and have, therefore, a perfectly definite significance.

molecular constitution, supported as it is by so many experimental results, provides substantial ground for specifying the shape of a molecule in relation to the atoms of which it is composed. According to this theory we should regard an atom of chlorine as being identical in arrangement with an atom of argon, except that its atomic number (or nuclear charge) is 17 instead of 18, and that, consequently, it lacks one electron in the outer shell required to complete the stable arrangement of eight outer electrons occurring in argon. Stability is secured in gaseous chlorine by the combination together of the atoms in pairs, thus forming diatomic molecules. In each pair two outer electrons are held in common, and, apart from possible distortion arising from such sharing, a chlorine molecule may be regarded as having the size and shape of two argon atoms in contact, *i.e.*, with the outer electron shells touching each other. Gaseous bromine is similarly related to double krypton atoms, and iodine to xenon. In the case of neon, the corresponding element is fluorine, for which there are no viscosity data in existence, but we may go one step further and make the comparison with oxygen. The atom of this gas has two less electrons than neon in the outer electron shell, but, in forming the molecule O_2 , the pair of oxygen atoms share four outer electrons. Thus, with the restrictions already mentioned, an oxygen molecule has the same size and shape as two neon atoms with their outer electron shells coincident.

The purpose of what follows is to test the validity of this view, making use of the combined results of X-ray crystal measurements and viscosity measurements of atomic and molecular dimensions. To be precise, we shall, for example, construct a hypothetical molecule by placing two argon atoms with their outer electron shells coincident, *i.e.*, with their centres separated by the distance $2.05 \text{ \AA}$, derived from crystal measurements. We shall then calculate what mean area (from the point of view of molecular collision) we should expect such a molecule to have, and compare it with the actual mean area of a chlorine molecule, deduced from the viscosity data of that gas. Identity between these two values and between values obtained similarly for the three other pairs of gases already mentioned, will justify the conclusion that the Lewis Langmuir view is substantially correct. It will at the same time—and this is equally important—establish quantitative agreement between the estimates of atomic dimensions derived from methods so different as the X-ray examination of crystals and the measurement of the viscosity of gases.

4. Consideration of Table I will make it clear that if, for example, two argon atoms have their outer electron shells coincident, the spheres representing their behaviour on the kinetic theory will overlap. For the centres are

then $2.05 \text{ \AA}$. apart, and the kinetic theory diameter is $2.87 \text{ \AA}$., a magnitude considerably greater. The same remark applies to the other monatomic gases, although the extent of overlapping varies from case to case. The question we have to answer is how such a pair will behave, in mutual collision with other pairs, from the point of view of kinetic theory. The hypothetical molecule so constituted will evidently be symmetrical about the line joining the atomic centres, and it will have a shape which we will consider in detail presently. Viewed from a direction making an angle θ with the symmetrical axis, it will present a certain area A , depending on the shape assigned to the molecule. Since all orientations of the axis are equally probable in thermally agitated molecules, the angle θ will occur with a proportional frequency $\sin \theta . d\theta$. Thus the mean area presented by the molecule will be

$$\bar{A} = \int_0^{\pi/2} A \sin \theta . d\theta. \quad (1)$$

This quantity, $\bar{A}$, will be equivalent to the expression $\pi\sigma^2$, which appears in the viscosity formula derived from the consideration of monatomic molecules as hard, elastic spheres. The evaluation of $\bar{A}$ will enable us to perform the comparison contemplated, viz., to test the dimensional equality of a hypothetical pair of contiguous argon atoms and a chlorine molecule, and the corresponding cases, neon-oxygen, krypton-bromine, and xenon-iodine.

5. We have now to consider the shape which we may assign to the molecule. It is known from Chapman's work on kinetic theory that, in the case of monatomic molecules, the model which fits in best with experimental facts is a hard elastic sphere* of definite radius σ . By analogy it is reasonable to suppose that a molecule, although not spherical, does behave in collision like a hard elastic body of some definite shape. That shape must evidently bear some relation to the value of σ for the participating atoms and to the distance apart, d , of the atomic centres. There are no means available at present for the precise calculation of the shape. All we can do is to assume probable shapes, and find which leads to the most consistent results. I have worked out these for three shapes for the contemplation of which there appear to be sound reasons, and the results differ so little from one another that we may feel justified in regarding the precise shape as relatively unimportant.

6. As a first approximation it will be presumably permissible to regard the molecule as a hard body formed by two overlapping hard spheres. In that case we may represent it by the full line figure in fig. 1. This figure actually shows to scale two argon atoms, but it will serve also to show qualitatively

* These hard spheres apparently exert a slight mutual attraction, but this property is neither opposed nor essential to our present argument.

the other pairs. The atomic centres O_1 and O_2 lie in the plane of the diagram and are separated by the distance $2d$, *i.e.*, the diameter of the outer electron

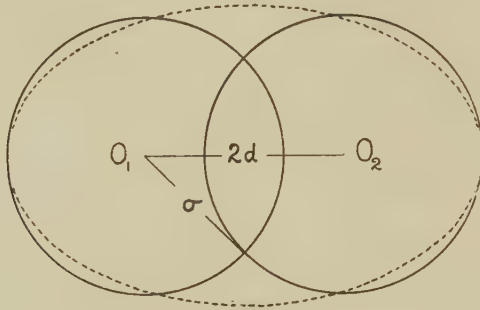


FIG. 1.

shell of each atom. The "kinetic theory" radius σ of each hard atomic sphere being greater than d , a certain fraction of the space is common, and the resultant shape is a sort of shrunk dumb-bell. If we view this solid figure from a direction making an angle θ with the axis O_1O_2 , it can be shown easily that the area A_1 presented is given by

$$A_1 = 2\sigma^2(\pi - \phi + \cos \phi \sin \phi),$$

where

$$\sigma \cos \phi = d \sin \theta. \quad (2)$$

According to (1) the mean area presented for all possible orientations is

$$\bar{A}_1 = 2\sigma^2 \int_0^{\pi/2} (\pi - \phi + \cos \phi \sin \phi) \sin \theta \cdot d\theta, ,$$

which, with the application of relation (2) can be put in the form

$$\bar{A}_1 = \pi\sigma^2 \left[1 + \frac{2K}{\pi} \int_0^{\pi/2} \{ \cos^2 \theta (1 - K^2 \sin^2 \theta)^{-\frac{1}{2}} + \sin^2 \theta (1 - K^2 \sin^2 \theta)^{\frac{1}{2}} \} d\theta \right],$$

where

$$K = \frac{d}{\sigma}.$$

This can be evaluated in terms of complete elliptic functions with the result,

$$\bar{A}_1 = \pi\sigma^2 \left[1 + \frac{4}{3\pi} \left\{ \left(\frac{1}{K} + K \right) \mathbf{E} \left(K, \frac{\pi}{2} \right) - \left(\frac{1}{K} - K \right) \mathbf{F} \left(K, \frac{\pi}{2} \right) \right\} \right], \quad (3)$$

from which, for any given value of K , $\bar{A}_1$ can be calculated in terms of $\pi\sigma^2$. Taking the values of K from Table I, $\bar{A}_1$ has been in each case deduced and recorded in Table II, column 3.

7. I am indebted to Prof. S. Chapman for the suggestion that it has to be remembered that the sphere of radius σ in the case of a single atom really represents a field of force, and that, therefore, when two such field interpenetrate the resultant field will be rounded off, so as not to exhibit the

discontinuity shown in the model just considered. He regards it as reasonable to represent the symmetrical diatomic molecule as an ellipsoid of revolution, having its long axis coincident with O_1O_2 . If we attribute to such a spheroid semi-axes a and c ($a > c$), it is easy to calculate the mean area which it presents. Denoting by A the area presented when viewed in a direction making an angle θ with the major axis, we can show that

$$A = \pi ac \left(1 - \frac{a^2 - c^2}{a^2} \cos^2 \theta \right)^{\frac{1}{2}},$$

whence, by (1), and putting $p^2 = \frac{a^2 - c^2}{a^2}$, which is of course less than unity,

$$\bar{A} = \pi ac \int_0^{\pi/2} (1 - p^2 \cos^2 \theta)^{\frac{1}{2}} \sin \theta \cdot d\theta.$$

This integration is readily performed and we obtain

$$A = \frac{\pi ac}{2p} (\phi_0 + \frac{1}{2} \sin 2\phi_0), \tag{4}$$

where

$$\sin \phi_0 = p = \left(1 - \frac{c^2}{a^2} \right)^{\frac{1}{2}}.$$

8. We have now to subject this spheroid to the conditions necessitated by the proximity of the atomic centres. It is, in the first place, reasonable to suppose that the major axis of the spheroid is equal to the extreme length of the overlapping spheres in fig. 1, *i.e.*, that

$$a = \sigma + d. \tag{5}$$

The second condition is not so easy to specify. Two aspects seem to be equally worthy of consideration, and for this reason both have been included. If we assume that the volume of the spheroid is equal to the sum of the volumes of the two spheres, the condition is

$$ac^2 = 2\sigma^3. \tag{6}$$

Alternatively, if we assume that the volume of the spheroid formed by the joining of the two atoms is less than the joint volume by that which is common to the two spheres, the condition proves to be

$$ac^2 = \sigma^3 \left[1 + \frac{3}{2} \frac{d}{\sigma} - \frac{1}{2} \left(\frac{d}{\sigma} \right)^3 \right],$$

or, remembering

$$K = d/\sigma,$$

$$ac^2 = \sigma^3 \left(1 + \frac{3}{2} K - \frac{1}{2} K^3 \right). \tag{7}$$

The principal sections of the first of these two alternative spheroids, in relation to the overlapping spheres, is shown by the dotted line in fig. 1. The other lies inside, too closely to be represented conveniently.

Combining equations (5) and (6) with equation (4), and denoting by $\bar{A}_2$ the value of A under these conditions, we obtain

$$A_2 = \frac{\pi \sigma^2}{p_1} \left(\frac{1+K}{2} \right)^{\frac{1}{2}} (\phi_1 + \frac{1}{2} \sin 2\phi_1), \tag{8}$$

where
$$p_1^2 = 1 - \frac{2}{(1+K)^3} = \sin^2 \phi_1;$$

whence the mean area presented by the spheroid of the first type can be calculated.

Similarly the combination of equations (5) and (7) with (4) give

$$\bar{A}_3 = \frac{\pi \sigma^2}{2p_2} (1+K)^{\frac{1}{2}} (1 + \frac{3}{2}K - \frac{1}{2}K^3)^{\frac{1}{2}} (\phi_2 + \frac{1}{2} \sin 2\phi_2), \tag{9}$$

where
$$p_2^2 = 1 - \frac{(1 + \frac{3}{2}K - \frac{1}{2}K^3)}{(1+K)^3} = \sin^2 \phi_2,$$

and $\bar{A}_3$ is the mean area presented by the spheroid of the second type.

The values of $\bar{A}_2$ and $\bar{A}_3$ for the four gases in Table I have been calculated, and are recorded in columns 4 and 5 of Table II. It will be seen by comparison of $\bar{A}_1$, $\bar{A}_2$, and $\bar{A}_3$, that the results obtained by the consideration of the three alternative models of the molecules are not large, the maximum difference being in the neighbourhood of 6 per cent. The importance of this will be considered later on.

Table II.—All areas in $\text{cm.}^2 \times 10^{-15}$.

Gas.	$\pi \sigma^2$.	$\bar{A}_1$.	$\bar{A}_2$.	$\bar{A}_3$.	Gas.	S.	$\bar{A}_1/S$.	$\bar{A}_2/S$.	$\bar{A}_3/S$.
Ne	0·435	0·67	0·70	0·65	O ₂	0·69	0·97	1·02	0·94
A	0·648	1·08	1·06	1·03	Cl ₂	1·07	1·01	0·99	0·96
Kr	0·797	1·34	1·31	1·28	Br ₂	1·28	1·05	1·03	1·00
X	0·970	1·66	1·60	1·57	I ₂	1·56	1·06	1·03	1·00

9. It is now possible to carry out comparisons with experimental results. In column 7 of Table II, I have recorded the effective mean areas (S) of the diatomic molecules O₂, Cl₂, Br₂, and I₂, using Chapman's formula and the best available viscosity data. For oxygen I have taken Chapman's own estimate, which is in remarkably close agreement with that which may be deduced from the recent viscosity measurement by Kia Lok Yen* in Millikan's laboratory. In the case of the halogen gases, I have used the data from my own experiments,† these being the only measurements avail-

* Kia Lok Yen, 'Phil. Mag.,' vol. 38, p. 582.
 † A. O. Rankine, 'Roy. Soc. Proc.,' A, vol. 86, p. 162; vol. 88, p. 575; and vol. 91 p. 201.

able. The last three columns show the respective values of the ratios $\bar{A}_1/S$, $\bar{A}_2/S$, and $\bar{A}_3/S$, and it will be noted that all these ratios are remarkably close to unity. The significance of this is important. It means that, for example, two argon atoms, with their outer electron shells coincident, would have a field of force which is almost identical with the actual field of force for a chlorine molecule, with the consequent deduction that the chlorine and argon atoms have equal size and shape. A similar argument applies to each pair of corresponding monatomic and diatomic gases.

10. It is worth while considering how the departures from unity in the ratios $\bar{A}/S$ may be accounted for. The maximum difference, whichever model we consider, is 6 per cent., and, if we confine our attention to the second model, *i.e.*, the spheroid of major axis $2(d + \sigma)$ and volume $\frac{4}{3}\pi\sigma^3$, the departure is reduced to a maximum of 3 per cent. It is quite possible that this may be accounted for by inaccuracy of the data upon which the calculations are based. Altogether apart from possible error in W. L. Bragg's figures, the calculation of S for the halogen gases, at any rate, is certainly liable to be inaccurate by a few per cent. For these gases, the viscosity measurements were, owing to experimental difficulties, carried out below the critical temperatures, that is, in a region of temperature where the kinetic theory of gases admittedly becomes inadequate. This consideration applies especially to bromine and iodine, in which cases it would alone, I think, account for the inconsistency in question. It is possible, also, that some allowance ought to be made for the distortion of the electron shells in atoms when they join to form molecules. Bearing these facts in mind, there seems to be considerable justification provided by the present investigation for making the following assertions:—

(a) There is substantial quantitative consistency between the estimates of atomic dimensions deduced from X-ray crystal measurement and from the kinetic theory of gases.

(b) In size and shape, the atoms of the monatomic inert elements are nearly indistinguishable from the atoms, respectively, of the neighbouring diatomic elements in the periodic table.

(c) The Lewis Langmuir molecular theory accounts satisfactorily for the kinetic behaviour of the molecules of oxygen, chlorine, bromine, and iodine in relation to the behaviour of the corresponding inert atoms, neon, argon, krypton, and xenon.

11. It has been already mentioned that the best model of the hard elastic body to which a molecule composed of two equal atoms is equivalent is a spheroid. The volume of this spheroid is equal to the sum of the volumes of the hard elastic spheres to which each participating atom is

separately equivalent. Apparently, the fields of force of the atoms, when they interpenetrate, rearrange themselves by bulging out in the equatorial plane, and contracting somewhat towards the poles, so as to preserve the same effective total volume. The other spheroid model, in which the total volume is diminished by the over-lapping volume, is not quite so successful. But both it, and more particularly, the first simple model contemplated (*i.e.*, a pair of overlapping spheres) give results which are reasonably consistent. This is fortunate, for it makes it possible to place some confidence in the extension of present theory to molecules in which the atoms are not equal. In that case the spheroid is an unlikely model, but we may still obtain results by methods, admittedly more laborious, based upon the model of overlapping spheres. This investigation the author hopes to carry out.

12. The case of nitrogen deserves special consideration. The molecule of this gas (N_2) has not been included in the above comparison because, according to Langmuir's theory, it is formed from two nitrogen atoms in a peculiar way. Each atom of nitrogen, if it could exist singly, is regarded as having only five electrons in the outer shell instead of the eight required to complete the stable neon arrangement. Langmuir represents these eight electrons as forming an octet or cube, and the joining of pairs of fluorine atoms to form F_2 , or pairs of oxygen atoms to form O_2 , by sharing electrons, presents no difficulty. In the former case, the deficiency of electrons being one per atom, the fluorine molecule attains the shape of two neon atoms in contact by the two shared electrons forming the common edge of the two cubes. In the oxygen molecule four electrons have to be shared by the atoms, and here the two cubes have a common face. With a deficiency of three electrons, however, as in the case of nitrogen, it is impossible for six electrons to be held in common without the complete disappearance of the linked neon cubes. In these circumstances, Langmuir regards the formation of the nitrogen molecule as being fundamentally different from the corresponding process in oxygen and fluorine. The interpenetration of the atoms is taken to be far greater, and involves a complete rearrangement of the electrons. The actual model given by Langmuir is a *single* enlarged electron cube of eight with *both* positive nuclei inside it. It is evident that this molecule has no resemblance at all to a pair of linked neon atoms, and it is most unlikely that its field of force, from the point of view of kinetic theory, will conform to any of the models we have considered. Indeed, if Langmuir's view is correct, a nitrogen molecule would be equivalent to a hard elastic body nearly spherical in shape, and the unmodified kinetic theory would apply to it with the same precision

as in the case of monatomic gases. Its atomic diameter, deduced from the viscosity of the gas, is 3.13×10^{-8} cm., which makes its mean area $S = 0.78 \text{ cm}^2 \times 10^{-15}$. This is considerably larger than any of the values of $\bar{A}$ for neon (Table II), and points to the fact that a nitrogen molecule does not resemble two linked neon atoms. In this negative sense, therefore, we again have corroboration of Langmuir's theory. For both points of view indicate that, whatever may be the actual arrangement of the nitrogen molecule, its mode of formation from two atoms is essentially different from that of its neighbour, the oxygen molecule.

13. In conclusion, I wish to express my gratitude to Prof. S. Chapman for reading the draft of this paper, and for making the suggestion—already referred to—which I have adopted.

On the Similarity between Carbon Dioxide and Nitrous Oxide.

By A. O. RANKINE, D.Sc., Professor of Physics in the Imperial College of Science and Technology.

(Communicated by Prof. H. L. Callendar, F.R.S. Received October 30, 1920.)

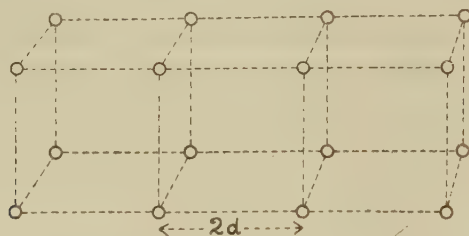
1. One of the most remarkable evidences in favour of the Lewis-Langmuir* theory of molecular constitution is the close degree of equality between nearly all of the physical constants of the two compounds, carbon dioxide and nitrous oxide. This identity is attributed by Langmuir to the arrangement of external electrons being the same for the molecules of the two gases in question. It is the purpose of the present communication to show that an appeal to the kinetic theory of gases, in conjunction with what is now known from W. L. Bragg's† work regarding the dimensions of atoms, produces substantial additional evidence in support of the Lewis-Langmuir views. In particular, it will be shown that the molecules of CO_2 and N_2O behave not merely as though they had the same size and shape, but as if each of them had an external electron arrangement practically the same as that of *three neon atoms in line and contiguous*.

2. This arrangement is precisely that which Langmuir suggests and is represented in fig. 1. A single neon atom is pictured as having eight outer

* I. Langmuir, 'Journ. Amer. Chem. Soc.,' vol. 41, p. 868 (1919).

† W. L. Bragg, 'Phil. Mag.,' vol. 40, p. 169 (1920).

electrons, presumably at the corners of a cube. Other atoms, although deficient in outer electrons, can, by forming molecules in which electrons are



Arrangement of outer electrons in the molecules CO_2 and N_2O . (after Langmuir.)

FIG. 1.

shared, attain a stable but multiple neon arrangement. Thus, if fig. 1 be taken to represent the molecule N_2O , it can be readily seen that the necessary conditions are fulfilled. The total deficiency of outer electrons is 8 (3 for each N atom and 2 for the O atom), and there are thus $24 - 8 = 16$ only available. These serve exactly to complete the arrangement shown, which is like three neon atoms with two faces shared. On the other hand, if the molecule is CO_2 , the electron deficiency is again 8 (2 for each O atom and 4 for the C atom), and the same arrangement therefore serves. There is no need, for our present purpose, to distinguish which cube represents any particular atom. The distribution of electrons is, according to Langmuir, externally equivalent to three neon atoms joined together, and is the same for both CO_2 and N_2O .

3. The data which W. L. Bragg (*loc. cit.*) has derived from X-ray crystal measurements enable us to specify how far apart are the centres of two neon atoms when they are brought so close together that their outer electron shells are contiguous. The distance in question is given by him as 1.30×10^{-8} cm. It is now proposed to construct a hypothetical molecule of three neon atoms with their centres in the same straight line, and successive centres 1.30×10^{-8} cm. apart, and compare its kinetic behaviour with that of the molecules of CO_2 and N_2O . The degree of correspondence will determine to what extent Langmuir's model is a correct representation of fact. The method employed is the natural outcome of that described by the author* in a previous paper, in which, among other things, the molecule O_2 was compared with two adjacent neon atoms. A single neon atom behaves, according to the kinetic theory of gases, like a hard elastic sphere which comes periodically

* A. O. Rankine (preceding paper).

into collision with other neon atoms. The diameter of this hard sphere, calculated by means of Chapman's* formula, and using the only available viscosity data,† proves to be 2.35×10^{-8} cm. This is considerably in excess of the distance 1.30×10^{-8} cm., which measures the distance between the centres of two neon atoms which are sharing outer electrons. Consequently, the hard spheres, to which each atom is separately equivalent from the point of view of mutual collision, will overlap in the manner indicated in fig. 2, which represents the three neon atoms we are considering, with

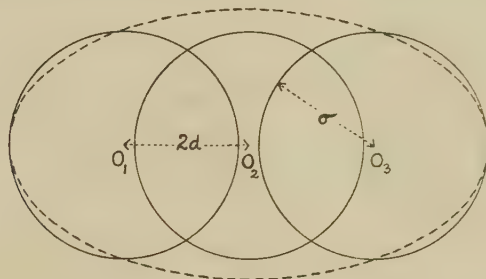


FIG. 2.

$2d = 1.30 \times 10^{-8}$ cm., and $2\sigma = 2.35 \times 10^{-8}$ cm. In applying the kinetic theory of gases to this hypothetical molecule we have, therefore, to recognise the molecule as not being spherical, and to estimate its collision frequency on this new basis. Put in another way, we have to find the average area, presented as a target by such a molecule, in terms of the corresponding area ($\pi\sigma^2$) for a single neon atom. This mean area we can then compare with the actual mean areas of the molecules of CO_2 and N_2O , as deduced from their viscosity data.

4. In my former paper, already referred to, I have made this calculation in the case of two equal overlapping spheres, treating them, as a first approximation, as a hard elastic body of that shape. If we denote by $\bar{A}$ the mean area presented by this body for all possible orientations of the axis, it was shown that

$$\bar{A} = \pi\sigma^2 + \pi\sigma^2 \cdot \frac{4}{3\pi} \left\{ \left(\frac{1}{K} + K \right) \mathbf{E} \left(K, \frac{\pi}{2} \right) - \left(\frac{1}{K} - K \right) \mathbf{F} \left(K, \frac{\pi}{2} \right) \right\}, \quad (1)$$

where $K = \frac{d}{\sigma} < 1$, and $\mathbf{F} \left(K, \frac{\pi}{2} \right)$ and $\mathbf{E} \left(K, \frac{\pi}{2} \right)$ are complete elliptic integrals of the first and second kinds, respectively.

The right-hand side of (1) is evidently made up of two parts: the first, $\pi\sigma^2$, being the complete area of projection of one of the spheres; and the

* S. Chapman, 'Phil. Trans.,' A, vol. 216, p. 279 (1916).

† A. O. Rankine, 'Roy. Soc. Proc.,' A, vol. 84, p. 181 (1910).

second part, which we will denote by $\bar{X}$, being the mean area of the crescent formed by the variable overlapping of the two spheres. If there are n equal spheres, equally spaced in a straight line, there will be $n-1$ crescents exactly similar—for a given orientation—to that just described. Consequently, the total mean area presented will be

$$\pi\sigma^2 + \overline{n-1} \bar{X}.$$

It is thus very easy to pass from the case of two spheres to that of any number equally spaced in line. In our present case the number $n = 3$, and the mean area, $\bar{B}$, becomes

$$\bar{B} = \pi\sigma^2 \left[1 + \frac{8}{3\pi} \left\{ \left(\frac{1}{K} + K \right) \mathbf{E} \left(K, \frac{\pi}{2} \right) - \left(\frac{1}{K} - K \right) \mathbf{F} \left(K, \frac{\pi}{2} \right) \right\} \right]. \quad (2)$$

Using the values of d and σ , already given as applicable to neon, we find that the mean area, which would be presented as a target by the hypothetical molecule contemplated, is

$$\bar{B} = 0.895 \times 10^{-15} \text{ cm.}^2. \quad (3)$$

5. An alternative model of the shape of the molecule has also been considered, namely, to treat it as an ellipsoid of revolution,* having its major axis coincident with the axis of the three spheres, as indicated by the dotted line in fig. 2. The results obtained for the mean area presented are

$$(a) \ 0.951 \times 10^{-15} \text{ cm.}^2,$$

and

$$(b) \ 0.853 \times 10^{-15} \text{ cm.}^2,$$

according as we take the volume of the spheroid as being equal to that of the three spheres, or to their total volume less the common portions. The dotted line in fig. 2 shows the principal section of the first of these spheroids; the second spheroid lies close inside, its minor axis being 0.91 of the first. The justification for substituting a spheroid for the three spheres does not appear to be so great as when there are merely two spheres, and it seems reasonable to rely on the value of $\bar{B}$ as given in (3) rather than on the alternatives (a) and (b), especially as $\bar{B}$ is the intermediate value. The comparison will therefore be carried out on this basis.

6. We have now to consider the actual values of the mean areas presented as targets by the molecules of N_2O and CO_2 . Chapman's (*loc. cit.*) formula may be used for the estimation of this mean area (which we will denote by $\bar{S}$), provided we know, in addition to the density of the gas, the number of

* The treatment of this problem differs in no essential way from that given in my former paper, and need not be repeated here. The magnitudes of the major and minor axes have merely to be determined on the new condition that there are three spheres instead of two.

molecules per cubic centimetre at N.T.P., the viscosity at a definite temperature, and the mode of variation of viscosity with temperature. For the densities of the two gases I have used the values corresponding to their molecular weights, the departures from "perfect gas" behaviour being negligible. For the number of molecules per cubic centimetre at N.T.P., Millikan's* modern value, 2.705×10^{19} , has been adopted. The viscosity data are more uncertain. There is little doubt about the absolute values of the viscosity (η_0) at 0°C. , but Sutherland's† constants (C) are not known with accuracy. I have relied, as far as possible, on modern determinations, and have taken for CO_2 the value $\eta_0 = 1.384 \times 10^{-4}$ C.G.S., which is the mean of Breitenbach's‡ estimate, 1.388×10^{-4} and Vogel's,§ 1.380×10^{-4} . For N_2O the value used is Vogel's, $\eta_0 = 1.362 \times 10^{-4}$ C.G.S. Only Von Obermayer's|| data are available for the calculation of C for the latter gas, and the value thus obtained is $C = 260$. In the case of CO_2 there have been several investigations of the variation of viscosity with temperature, the principal ones being Holman's,¶ Von Obermeyer's, and Breitenbach's. The latter gives the value $C = 239$, and this is supported by calculations from Von Obermayer's figures. On the other hand, Sutherland obtains the value $C = 277$ from Holman's data. The estimate I have used is $C = 249$, which is the same as that adopted by Chapman (*loc. cit.*), but it is evident that some uncertainty still exists.

On the basis of the above data, the values obtained for the mean target areas of the molecules of the two gases are:—

$$\text{CO}_2, \quad \bar{S} = 0.870 \times 10^{-15} \text{ cm.}^2,$$

$$\text{N}_2\text{O}, \quad \bar{S} = 0.867 \times 10^{-15} \text{ cm.}^2.$$

Too much stress must not be laid on the precision of the equality of these two figures. Each is quite possibly subject to an error of something like 5 per cent., on account of uncertainty regarding Sutherland's constant. Within the limits of experimental error, however, the molecules of CO_2 and N_2O do behave, in the gaseous state, as though they were of identical size and shape.

7. The comparison of $\bar{S}$ with the mean target area, $\bar{B}$, of the hypothetical triple neon molecule is shown in the following Table.

* R. A. Millikan, 'Phil. Mag.,' vol. 34, p. 1 (1917).

† W. Sutherland, 'Phil. Mag.,' vol. 36, p. 507 (1893).

‡ P. Breitenbach, 'Ann. der Physik,' vol 5, p. 166 (1901).

§ H. Vogel, 'Berlin Diss.' (1914).

|| A. von Obermayer, 'Sitz. Akad. Wien,' vol. 73, p. 433 (1876).

¶ S. Holman, 'Phil. Mag.,' vol. 21, p. 199 (1886).

Table I.—All areas in $\text{cm}^2 \times 10^{-15}$.

Gas.	$\bar{S}$.	$\bar{B}/\bar{S}$.
Carbon dioxide	0·870	1·03
Nitrous oxide	0·867	1·03
$\bar{B} = 0·895$		

In both cases the ratio $\bar{B}/\bar{S}$ is seen to differ by only 3 per cent. from unity. We can, therefore, conclude that not only have the molecules CO_2 and N_2O the same molecular dimensions, but that their behaviour is, within the limits of experimental error, consistent with the assumption that in both cases the dimensions are those of three neon atoms in line with contiguous outer electron shells.

Experiments on Electron Emission from Hot Bodies.

By SIH LING TING, M.Sc., Birmingham.

(Communicated, with a Preface, by Prof. O. W. RICHARDSON, F.R.S.)

(Received May 6, 1920.)

PREFACE.

The first measurements* of the kinetic energy of the electrons emitted from hot bodies were made by myself, partly in collaboration with Dr. F. C. Brown, in 1907–1909. The completed experiments were practically confined to platinum as a source of emission, largely on account of technical difficulties experienced with other materials. These experiments showed that the velocity distribution among the emitted electrons was in close agreement with Maxwell's law of distribution for a gas, of molecular weight equal to that of the electrons, in thermal equilibrium at the temperature of the source. This applies both to the component of velocity normal to the emitting surface and to that in a perpendicular direction. In the simple unidimensional case, where the cathode and anode form parallel planes of indefinite extent, the current, i , which flows against a retarding potential, V ,

* 'Phil. Mag.,' vol. 16, pp. 353, 890 (1908); vol. 18, p. 681 (1909).

depends only on the normal velocity component, and with Maxwell's distribution is given by

$$i = i_0 \exp.(-\alpha V), \quad (1)$$

where $\alpha = e/kT$, e being the electronic charge, k the Boltzmann constant, T the absolute temperature, and i_0 the current when $V = 0$. The inverse of the factor α is in fact a measure of the energy with which the electrons are ejected from the surface.

The experiments showed that, with platinum under a very considerable variety of conditions, the exponential equation was obeyed with considerable accuracy. The average of eight determinations of k/e by this method agreed with the theoretical value to within a fraction of 1 per cent.,* although the individual determinations differed from the average by almost 20 per cent. These variations were undoubtedly large, and in excess of expectation from any obvious source of experimental error. At the same time, these experiments were subject to a number of defects such as might arise from (1) inequalities in the temperature of the source, (2) unsatisfactory methods of determining these temperatures, (3) the difficulty of realising a truly plane surface of hot metal, and (4) the presence of the electric and magnetic fields caused by the electric currents used in heating the source. In view of these and other known sources of uncertainty, the foregoing experiments, as a whole, were taken to indicate that the electrons emitted from platinum under the conditions to which the tests were subjected, possessed a velocity distribution in accordance with Maxwell's law.

On the other hand, some preliminary tests made (1) with platinum saturated with hydrogen, (2) with platinum coated with lime, and (3) with the liquid alloy of sodium and potassium, seemed to show the presence of velocity distributions having no very close resemblance to Maxwell's law. These experiments had to be abandoned without the facts being fully ascertained, owing to the pressure of other problems.

In 1914 the subject was attacked by Schottky† who utilised the case of coaxial cylinders presented by a filamentary cathode of circular section and a concentric cylindrical anode. This structure has important practical advantages. The effects of the magnetic and electric fields of the current used to heat the filament were avoided by an interrupted current method due to v. Baeyer. Schottky's experiments were made with carbon and tungsten, and the data were in good agreement with the requirements of Maxwell's law except that the average energy of the emitted electrons was in every case in excess of the value calculated from the temperature of the source. This,

* Richardson, 'Emission of Electricity from Hot Bodies,' p. 146.

† 'Ann. der Physik,' vol. 44, p. 1011 (1914).

however, was estimated from the value of the saturation current in comparison with the emission data given by other authors. In view of the known large effect on the emission of traces of certain possible contaminants this method involves an element of uncertainty; so that one cannot be sure whether the discrepancy exceeds the probable error or not.

The experiments made by Mr. Sih Ling Ting which are described in the sequel were commenced in 1917 at my suggestion in order to try to clear up some of these matters. It was planned first to investigate the behaviour of tungsten using some independent check on the temperature of the filaments and then to investigate the substances whose behaviour had been recorded as abnormal in 1909. Whilst the work is incomplete it is necessary to publish an account of what has been accomplished up to the present, as Mr. Ting is returning to China. I propose to continue it from the present stage with other help.

The following experiments, which I have directed and closely followed throughout, show that whilst Maxwell's law of velocity distribution may be an ideal which is realised in some cases, it is a condition of affairs which is frequently departed from in practice. A very common type of emission appears to be one in which the distribution of velocity is in close agreement with the requirements of Maxwell's law except that the average kinetic energy is about twice that which would correspond to the temperature of the source. Some of the platinum data, however, exhibit velocity distributions which are not at all of the Maxwell type. It may be that the Maxwell type would hold for an ideal flat surface of pure metal and that these variants from it are conditioned by effects of absorbed gas or the like. Some support for such a view may be drawn from the hysteretic effects described by Mr. Ting in Part III, as such effects are generally due to the action of gas films. On the other hand the tubes used by Mr. Ting were undoubtedly freed more thoroughly from gases and the vacua were better in all respects than those I experimented with in 1908. It is hoped that further experiments will indicate more precisely the connection if there is one between the changes in the velocity distribution and the gas actions referred to.

I wish to express my thanks to the Department of Scientific and Industrial Research for a grant which rendered possible the carrying out of the later part of the experiments described in the sequel.

O. W. R.

EXPERIMENTS ON THE VELOCITY DISTRIBUTION OF THE EMITTED ELECTRONS
FROM INCANDESCENT FILAMENTS.*Introduction.*

Broadly speaking, the method of investigation consists in measuring the electron current from the hot body to a neighbouring electrode against various opposing potential differences. These currents are calculable on the assumption that Maxwell's law of velocity distribution applies to the emitted electrons. In the case of parallel plane electrodes they are then given by equation (1); for a hot wire of circular section and a concentric cylinder they are given by an equation* which, provided the ratio of the two radii is sufficiently great and the opposing voltage is not too small, reduces to

$$i = i_0 \frac{2}{\sqrt{(\pi)}} \left\{ \sqrt{(xV)} e^{-xV} + \int_{\sqrt{(xV)}}^{\infty} e^{-x^2} dx \right\}. \quad (2)$$

These conditions as to the ratio of the radii and the magnitude of the voltage were satisfied in the relevant experiments in the sequel. The logarithms of i/i_0 calculated from (1) and (2) are graphed against xV in fig. 1A. Except near $xV = 0$, equation (2) gives practically a straight line, whose slope differs about 10 per cent. from that given by (1). By comparing the theoretical with the experimental curves for any particular structure we are enabled to judge if, and to what extent, Maxwell's law is satisfied.

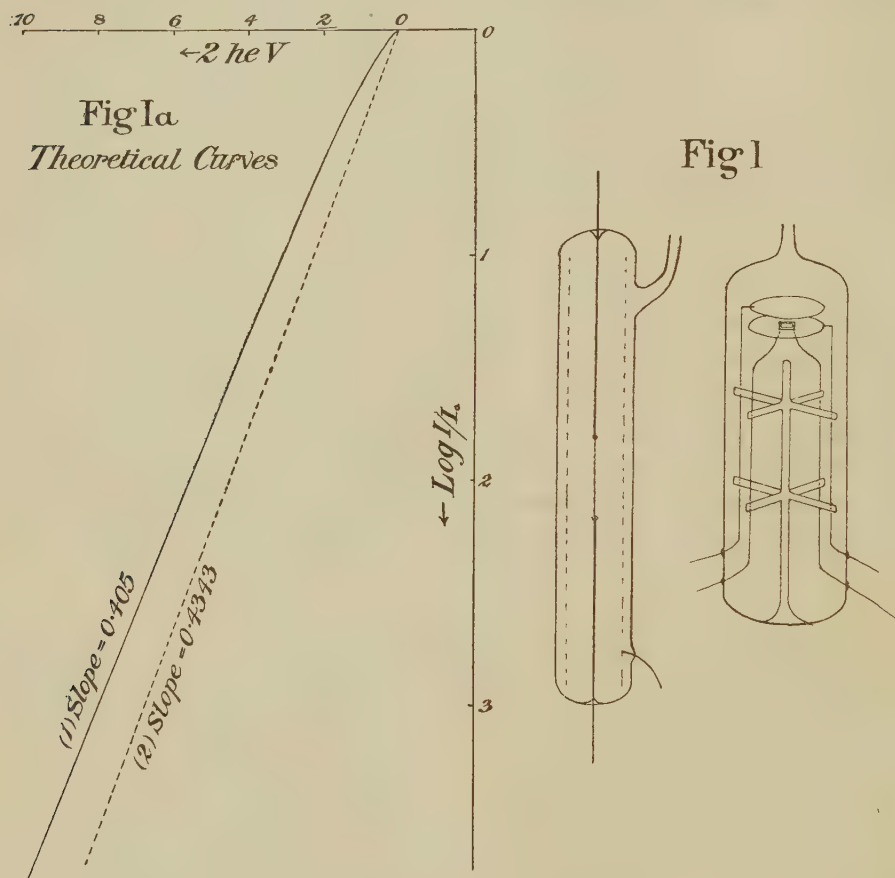
Methods and Principle of the Experiments.

(a) *Preparation of the Tube.*—The forms of the tubes used in the experiments are shown in fig. 1. In the case of the cylindrical field the filament is a short wire held between two thick copper leads. The concentric cylindrical electrode is made of copper wire gauze. For the uniform field the filament is a narrow platinum strip. Two thick platinum foils are used for the two parallel plates. All other metallic parts in this case are also made of platinum, so that the tube can be cleaned by boiling nitric and hydrochloric acids in it. The tube is exhausted in a vacuum furnace, as described by Prof. Richardson in his book ('The Emission of Electricity from Hot Bodies'), by a Gaede mercury pump for about five hours a day for four days. During the exhaustion the temperature of the furnace is kept at about 750° absolute, so that all gases in the wall of the tube and the massive parts of the apparatus may be driven out and pumped off. Liquid air is then placed around the charcoal tube condenser for more than ten hours. While the condenser is still in liquid air the filament is glowed out by a strong electric

* Schottky, *loc. cit.*

current for a few minutes, and after about half an hour's interval the tube is then sealed off from the pump. In some cases another charcoal tube condenser is attached to, and exhausted with, the filament tube, and can be immersed in liquid air when observations on thermionic current are being taken.

(b) *Measurement of Thermionic Current.*—Four different arrangements were



used, shown in figs. 2-5. In these diagrams, A is an ammeter for recording the heating current, K or K' a revolving commutator, G' a galvanometer in the Wheatstone bridge used for measuring the temperature, G a galvanometer for measuring the thermionic current, B', P and V a battery, slide wire, and voltmeter, for regulating and measuring the applied potential difference; k, k' are keys such as are used in electrostatic measurements, and E denotes an earth connection.

Method (1), fig. 2, is the arrangement substantially as described by

Schottky. Method (2), fig. 3, shows this method modified to measure small thermionic currents with a sensitive electrometer. The important innovations consist in (a) using two separate commutators, K and K' , which, however, are kept in the right phase relation by revolving on the same axis; (b) the device $J C, J' C'$, which enables the potential of the hot wire to be raised continuously by an amount equal to that of the electrometer, thus maintaining a constant potential difference between the filament and the cold electrode during each measurement. Method (3), fig. 4, has the first

Fig 2

Method (1)

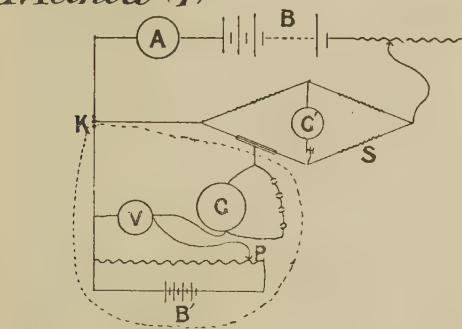


Fig 4

Method (3)

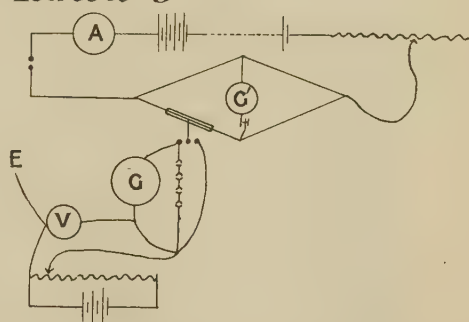


Fig 3

Method (2)

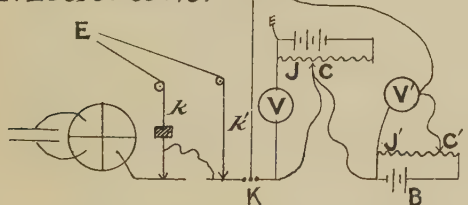
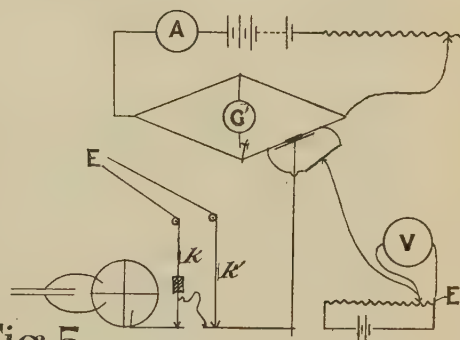


Fig 5

Method (4)



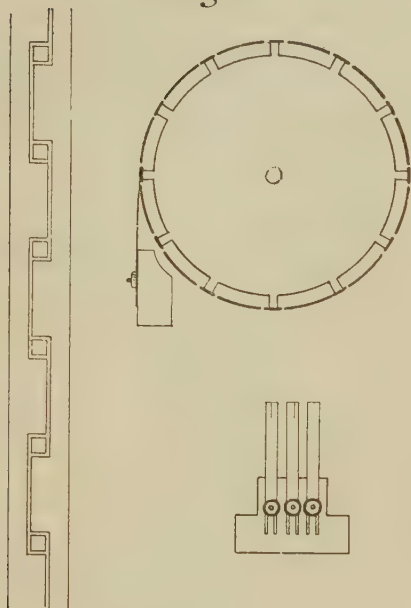
feature of Method (2) applied to Method (1). Method (4), fig. 5, is the old arrangement substantially as described by Richardson and Brown.

(c) *Estimation of the Temperature.*—Under the condition of a balance of the Wheatstone bridge, the resistance of the filament can be calculated, and hence the temperature can be deduced. For platinum wire and strip, the temperature was taken simply as proportional to the resistance in the actual estimation, and, for tungsten wire, the data given by Langmuir* were made use of.

* 'Phil. Mag.,' vol. 7, No. 3 (March, 1916).

From the fact that the filament is heated by current which is interrupted by the commutator (fig. 6), and actually stops for more than half the time, the

Fig 6



question arises whether the temperature drops appreciably during the short interval of a break (the commutator makes 150 to 200 breaks per second). Such doubt is, however, removed by the following two tests. A large accelerating potential difference was put on between the filament and the electrode to produce a saturation current. The electrode was connected, not through the commutator, but directly to the galvanometer. The filament was then heated, first by a continuous current, and then an interrupted current to the same temperature as indicated by equal resistance. It was found that the readings of the thermionic currents in the two cases were practically identical. The second test was to compare the temperatures

deduced from the saturation current and the resistance. A temperature and saturation current curve was obtained from preliminary observations with the same filament, using continuous heating current. The temperatures were deduced from the corresponding resistances. From this curve, the temperature of the filament, when heated by interrupted current, could be deduced from the saturation current. Account must be taken, of course, of the fact that, when the switch is used, the observed thermionic current is only a fraction of the total emission.

Results of the Experiments.

(a) *Tungsten Wire in Cylindrical Field.*—Three tubes were used in the experiments. With the first tube, five experiments were first made at different temperatures, using the galvanometer for the measurement of current. In some cases two readings of the current for each potential were taken, one when the potential was being increased, and another when it was being decreased. Where there was any difference between the two, which was never very great, the mean value was always taken. When there was only one reading taken, the current was allowed to become steady. The

filament was then strongly heated by a current for a few hours, and two more observations were made. The result of all the experiments shows that the I-V curves are all logarithmic in character, but the slope of the log I-V curves is in each case only about half the value calculated from the temperature in accordance with Maxwell's law, as may be seen from the following Table :—

Table I.—First Tube (thin filament). Method (1).

Diameter of filament 0.00549 cm.; length of filament 6.83 cm.; diameter of cylinder 2.2 cm.; length of cylinder 12.5 cm.

Temperature.	Approximate saturated current.	Slope of log I-V Curve.		Ratio S/S'.
		S (experimental).	S' (theoretical).	
K.	mm.			
1455	101	1.63	3.17	0.51
1475	161.5	1.60	3.12	0.51
1500	241.5	1.60	3.07	0.52
1528	464	1.60	3.02	0.53
1574	1015	1.55	2.92	0.53
(After Heating.)				
1574	224	1.73	2.92	0.59
1626	487	1.69	2.85	0.59

In the above Table the current is expressed in terms of the galvanometer readings (1 mm. $3.46 \cdot 10^{-8}$ ampères). The current was greatly reduced after the strong heating. But the logarithmic nature of the curve was found unaltered, though the value of the slope seemed thereby slightly increased. The general character of the curves can be seen from figs. 7a and 7b, where the result of the first five experiments are represented. The curve shown by the dotted line is the theoretical curve for temperature 1455 K.

The second tube was made exactly like the first. The filament was of the same wire. Altogether, seven experiments were made. The first four were made with the galvanometer at temperatures ranging from 1400 K to 1700 K. Method (3) was used. The last three were made with the electrometer at lower temperatures, using Method (2). The temperatures of the filament in the first four experiments were estimated also from the saturation current, and were found in good agreement with the values calculated from the resistance. As in the case of the first tube, all the curves obtained are logarithmic, and the slope is only about half of the theoretical value.

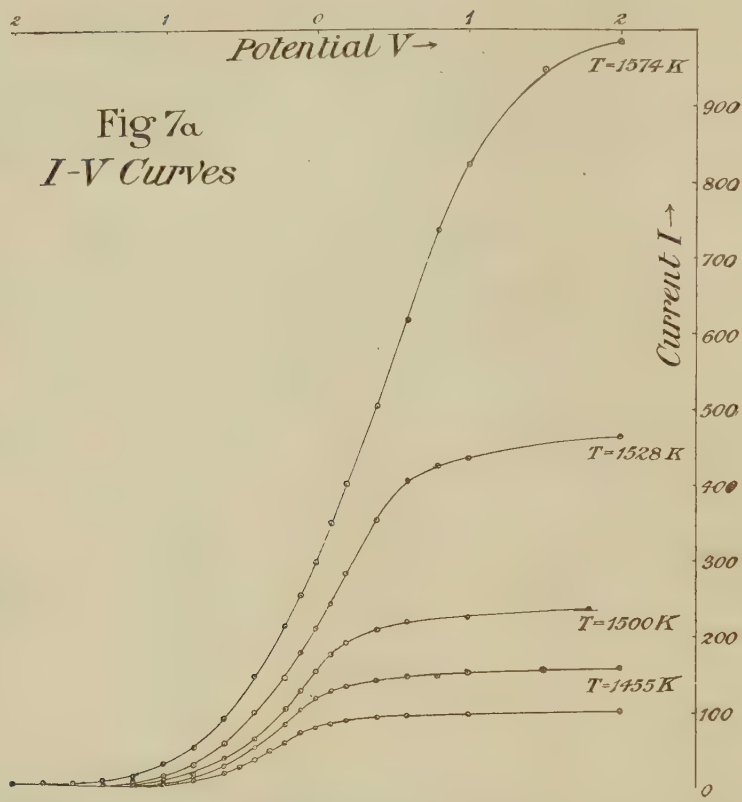


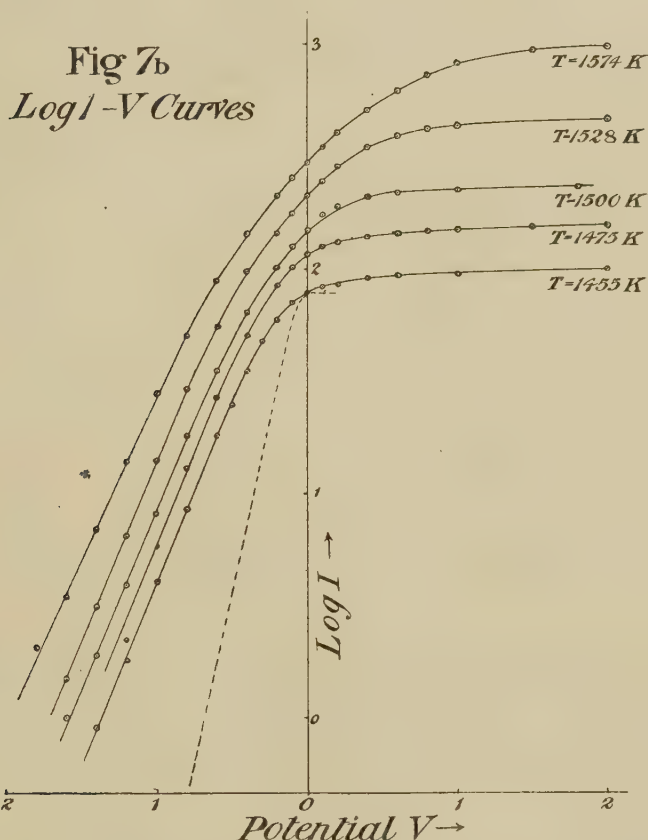
Table II.—Second Tube (same wire). Methods (2) and (3).

Temperature.		Slope.		S/S'.
From resistance.	From saturated current.	S (experimental).	S' (theoretical).	
K.				
1700	1703	1·2	2·71	0·44
1600	1600	1·3	2·88	0·45
1500	1490	1·45	3·07	0·47
1400	1360	1·8	3·29	0·55
1100	—	2·3	4·18	0·55
1080	—	2·6	4·26	0·61
1060	—	2·8	4·34	0·65

The above Table shows clearly that the slope S increases with decrease of temperature, and the ratio S/S' is not far from half in all cases. The curves for the first four experiments are similar to those shown in fig. 7; those for the last three experiments are shown in fig. 8. One difference between these curves and all the others should be noted, namely, the

current attained saturation when there was still a resisting potential difference between the filament and the electrode of about 0.7 volt.

The same result was found with the third tube. The filament was a thicker wire. Method (2), with the electrometer, was used. The value of the ratio S/S' obtained was 0.49 for temperature 1030 K.



(b) *Platinum Wire in Cylindrical Field.*—In this case an improved form of the tube was used, to minimise the error due to the escape of the electrons from the open ends of the electrode and the falling off of the temperature at the ends of the filament. The filament used was a long platinum wire, and the electrode consisted of three separate parts, of which only the middle was connected to the current-measuring instrument; the other two simply served as “guard-rings.” The result is shown in the following Table and in fig. 8a.

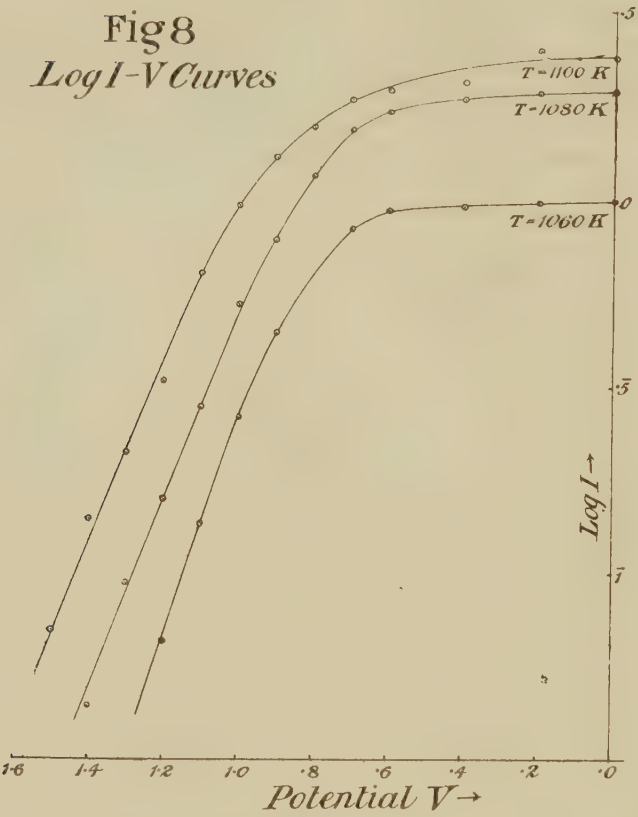


Table III.—Tube with Long Filament and Short Electrode. Method (2).

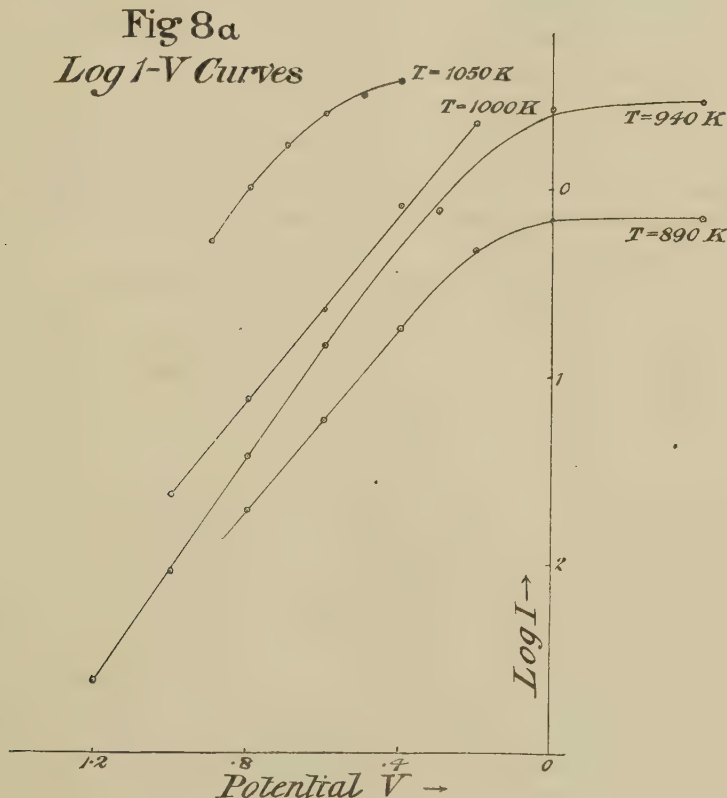
Temperature.	Slope S (experimental).	Slope S' (theoretical).	Ratio S/S'.
890 (1)	2.3	5.2	0.44
910 (3)	2.9	5.1	0.57
940 (2)	2.9	4.9	0.59
975 (5)	2.3	4.7	0.49
1000 (4)	2.46	4.6	0.53
1050 (6)	—	4.4	—

The values of the temperature in the Table are only approximate. The curve for the last experiment is not quite straight, owing to the high temperature and the great current. The value of S and the ratio S/S' do not change regularly with the temperature, as in the case of the tungsten filaments. This is probably due to the fact that the experiments were not made in the order of the temperature, but in the order as indicated by the numbers in brackets, and were not made one immediately after another.

From all the experiments described above, both with tungsten and platinum filaments in a cylindrical field, we can draw the conclusion that, practically in every case, we have—

(1) A logarithmic curve if the values of the thermionic current are plotted against the corresponding values of the potential difference between the filament and the electrode; and

(2) The slope of the curve with the logarithms of the values of the current against the values of the potential difference is equal to only about half of the



value as required on the assumption that the velocities of the emitted electrons are distributed in accordance with Maxwell's law, or in other words, the actual velocity distribution corresponds to a temperature about twice as high as the actual temperature estimated from the resistance of the filament.

(c) *Platinum Strip in Uniform Field.*—Before the tube (fig. 1) was joined to the pump it was boiled with nitric and hydrochloric acid, each for about two hours, and then cleaned with distilled water. In the first series of experiments the tube was left on the pump which was working continuously

when observations on the thermionic current were made. No liquid air was applied to the charcoal tube condenser. The curves of the first few experiments were varying owing to the positive current present which, at the beginning, was as great as the negative. By continuously heating the filament with a large electric force to drive it off it slowly died down. When it disappeared entirely the curve assumed the characteristic logarithmic form. When the pressure in the tube was higher than $1/100$ of 1 mm. of Hg the curve was no longer consistent but when the pressure was fairly low and no positive current was present the I-V curve was logarithmic. The strength of the current, however, was found to decrease by heating. The results of four experiments under such conditions are given below.

Table IV.—First Tube with Platinum Strip. Method (4).

Diameter of platinum plate 2.5 cm. (about); distance between plates 0.5 cm. (about); dimension of the rectangular hole = 5×2 sq. mm.

Temperature.	Slope S (experimental).	Slope S' (theoretical).	Ratio S/S'.
1466	1.7	3.46	0.49
1460	1.89	3.47	0.53
1450	2.1	3.5	0.60
1500	1.85	3.88	0.55

The same tube together with the attached charcoal tube condenser was then put in the vacuum furnace, and heated and exhausted in the manner described before. When the tube was finally sealed off from the pump the charcoal tube condenser was immersed in liquid air during all the experiments. In the first experiment at the very beginning no positive current was found. The curve was logarithmic and gave a much larger value for the slope. In fact the value was not far from that required by Maxwell's law. But immediately after the first experiment the thermionic current was found to be decreasing. At the same time the curve lost its logarithmic character. The decreasing of the current was more rapid at first and became slower and slower. The shape of the curve, however, remained more or less unaltered. The removal of the liquid air from the condenser did not make any difference either in the strength of the current or the shape of the curve. The filament finally burnt off after many hours' continuous heating.

The second tube was made exactly like the first with the old electrodes and a new strip. It was treated in the same way and the experiments were carried out under the same conditions. The result obtained entirely agreed with that of the first tube; namely, the thermionic current decreased first.

rapidly and then slowly, the curve changed from a logarithmic character to a different one. How the current dropped down in the first half-hour may

Fig 9
I-V Curves



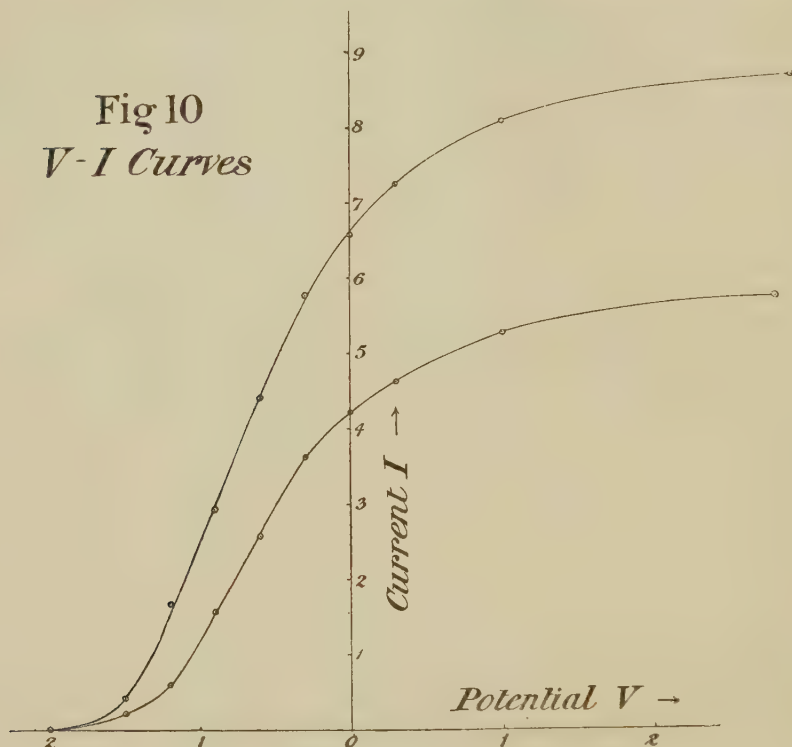
be seen from the curves in fig. 9 where the three observations were made one after another at the same temperature with only a few minutes' interval. The final shape of the curve, when the current had become more or less steady, is shown in fig. 10. The lower curve was taken six hours after the top one, the temperature being the same.

The result of the above experiments with platinum strips in a uniform field points to the conclusion that in tubes at pressure of the order of 10^{-3} mm. Hg the electrons emitted by a platinum strip have the same property in regard to velocity distribution as those emitted by platinum and tungsten wires. But this property disappears with the simultaneous decrease of the thermionic current in tubes which have been baked and exhausted in the vacuum furnace, and which have an attached charcoal tube condenser immersed in liquid air when the filament is heated during the experiment.

It may be mentioned in this connection that the thermionic current in the experiments with tungsten wires remained very constant for hours and no positive current was ever detected.

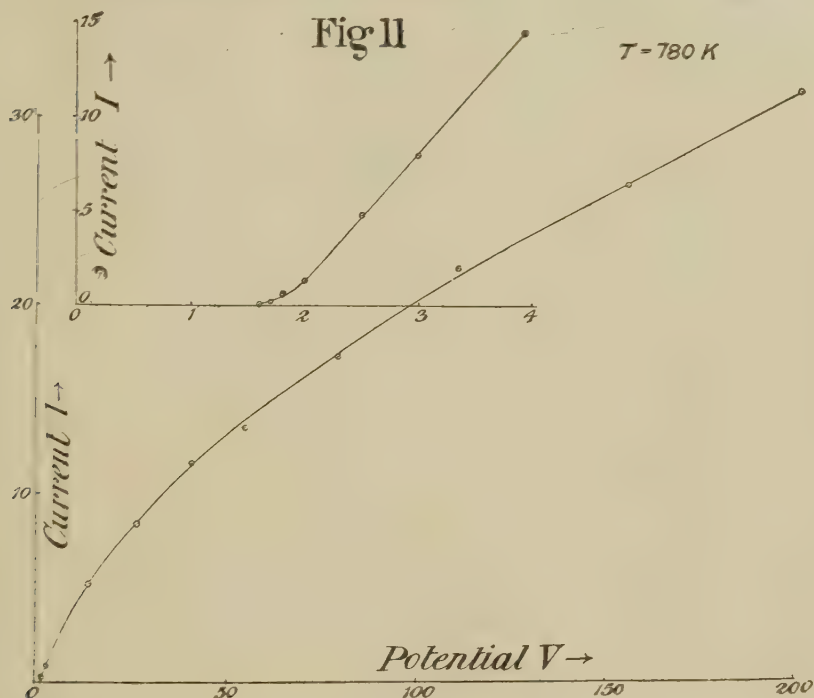
(d) *Platinum Filament Coated with Chemical Compounds.*—The tube used

Fig 10
V-I Curves



was of the type of a long wire surrounded by a short cylindrical electrode with "guard-rings." Make-and-break switches were used. The first tube was coated with barium and strontium oxides. In the experiment with this filament the thermionic current was found measurable by a sensitive galvanometer when the filament was only very dull red hot. When the electrometer was used the filament was hardly visible in the dark. The most striking feature is, however, the inertness of the electrons emitted. To get a measurable current some driving force is generally required, except at very high temperatures, and even then the current does not increase appreciably until the potential difference is increased to about 1 volt. Generally speaking the current starts when more than 1 volt potential is put on, but at about 600 K. in one of the experiments a potential of 2 was found necessary. The other important feature is the difficulty of saturating the current. The current generally increases with the driving potential up to from 100 to

200 volts without showing any tendency towards saturation. The results of one experiment are shown in fig. 11. The top curve shows the beginning part of the lower one on a larger scale. All the other curves are similar to this. Similar results were obtained from a wire coated with lime, obtained by evaporating drops of pure $\text{Ca}(\text{NO}_3)_2$ solution on the filament.



Observations on Hysteretic Effects in Thermionic Electron Currents.

During some experiments on the velocity distribution of the electrons emitted from tungsten wire, in which the thermionic current was measured for various potential differences between the emitting filament and the surrounding electrode, a curious effect was observed in regard to changes of the current with time. It was found that so long as the potential difference was small or was so directed as to resist the emitted electrons the thermionic current had a definite value for each potential difference; but when a large accelerating potential difference was put on, the current changed with time and only settled down to a steady value after a considerable time. The initial value of the current often differed considerably from the steady value, and was greater or smaller than the steady value according to whether the previous potential difference was greater or smaller; or, to be more exact, according to whether the current for the previous potential difference was

greater or smaller. This distinction must be made because it was found that greater potential difference did not necessarily produce greater current; but, on the contrary, the current showed a maximum at certain points, beyond which it decreased.

The experiments were made with long glass tubes, each of which had a short tungsten filament, of about 2 to 3 cm. length, and a concentric cylindrical electrode, of about 10 cm. length and 2.5 cm. diameter, made of copper wire gauze. The tube was exhausted and heated in a vacuum furnace for about

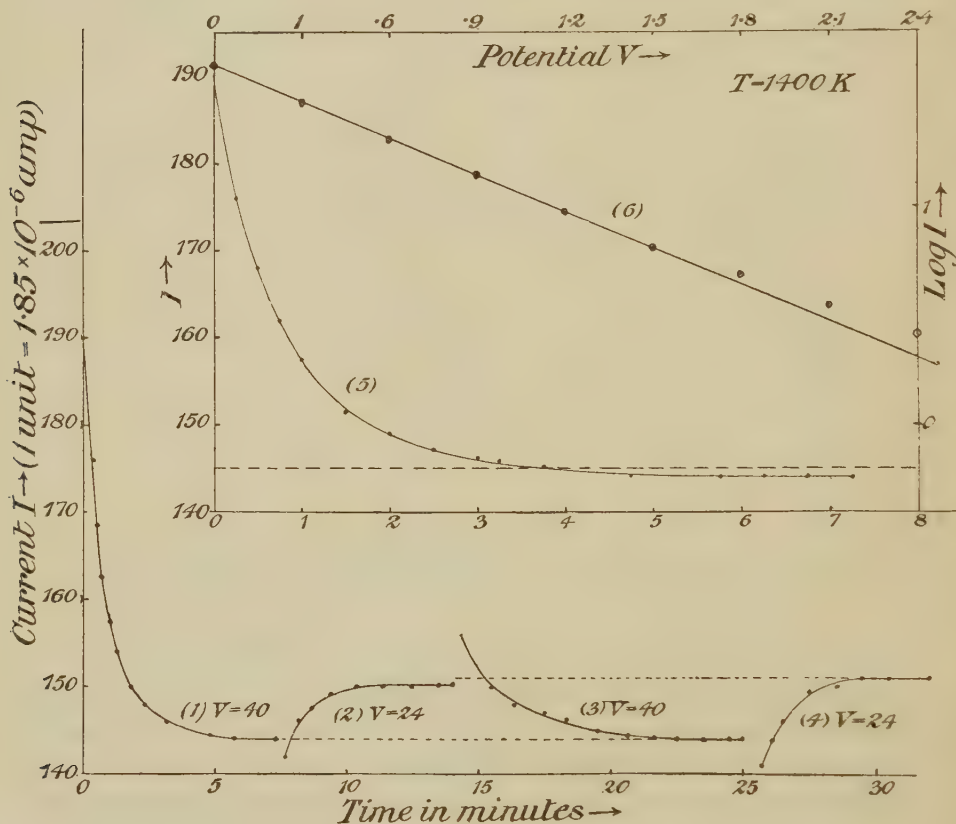


FIG. 12.

twenty hours. Before it was sealed off from the pump the charcoal tube condenser in connection with the pump was put in liquid air for a long time and the filament was glowed out by a strong current. To take observations of the thermionic current, the filament, which formed one arm of a Wheatstone bridge, was heated by an electric current. One end of the filament was earthed and the electrode was then charged to different potentials. The current was measured by a sensitive galvanometer. In the

first experiment a potential of 40 volts was put on the electrode when the temperature of the filament became constant. The current started with a certain initial value, but decreased, first rapidly then slowly, and finally settled down to a steady value after about seven minutes. The potential was then changed to 24 volts. The current dropped a little at the beginning, but rose to a greater value than for 40 volts, when it became steady again. In order to make sure that the increase of the current was not due to a change

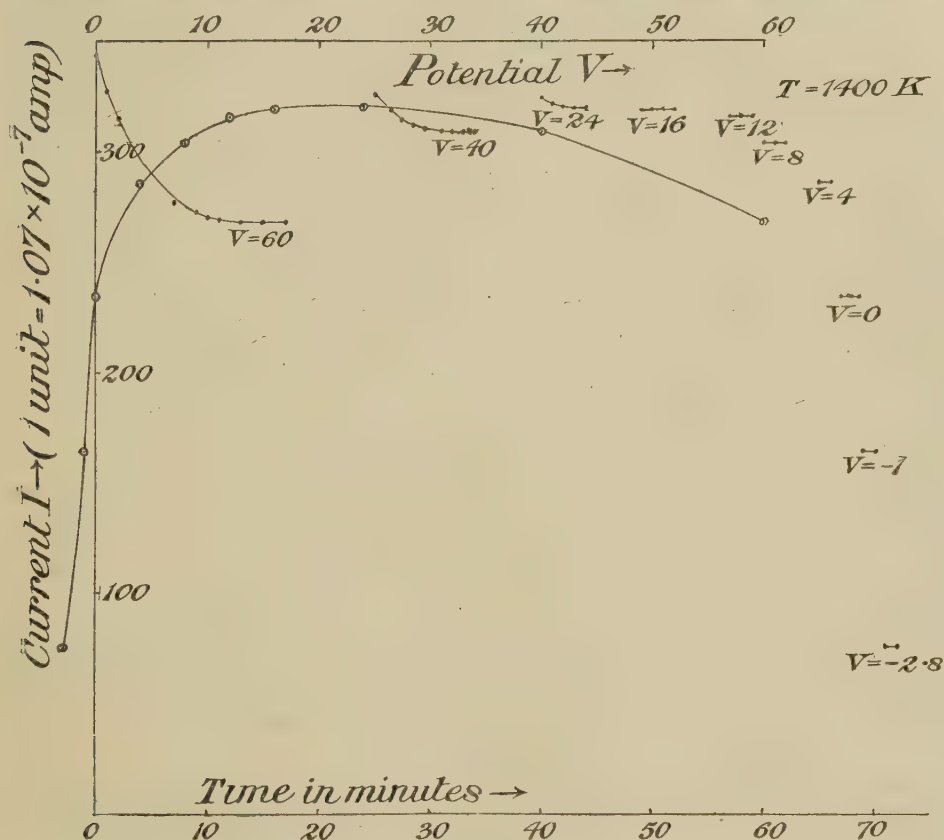


FIG. 13.

of the emission, the potential was changed back again to 40 volts. At once the current increased, but soon fell down to its former steady value for that potential. Only the initial value this time was much less than for the first time. On changing the potential once more to 24 volts, the same phenomenon repeated itself. The result of the experiment is shown in fig. 12, where the curves are plotted with current against time. From these curves we see clearly that (1) there was a definite steady value of the current for

each potential, and the value for 24 volts was decisively greater than that for 40 volts; (2) the initial value of the current was influenced by the previous potential in the way indicated above. Curve 5 in the same figure is simply curve 1 on a larger scale, and curve 6 is plotted with the logarithm of the excess of current above the dotted line against time. The latter as shown is nearly a straight line.

The object of the second experiment, which was made with the same tube, was to find the steady value of the current at a number of potentials. To

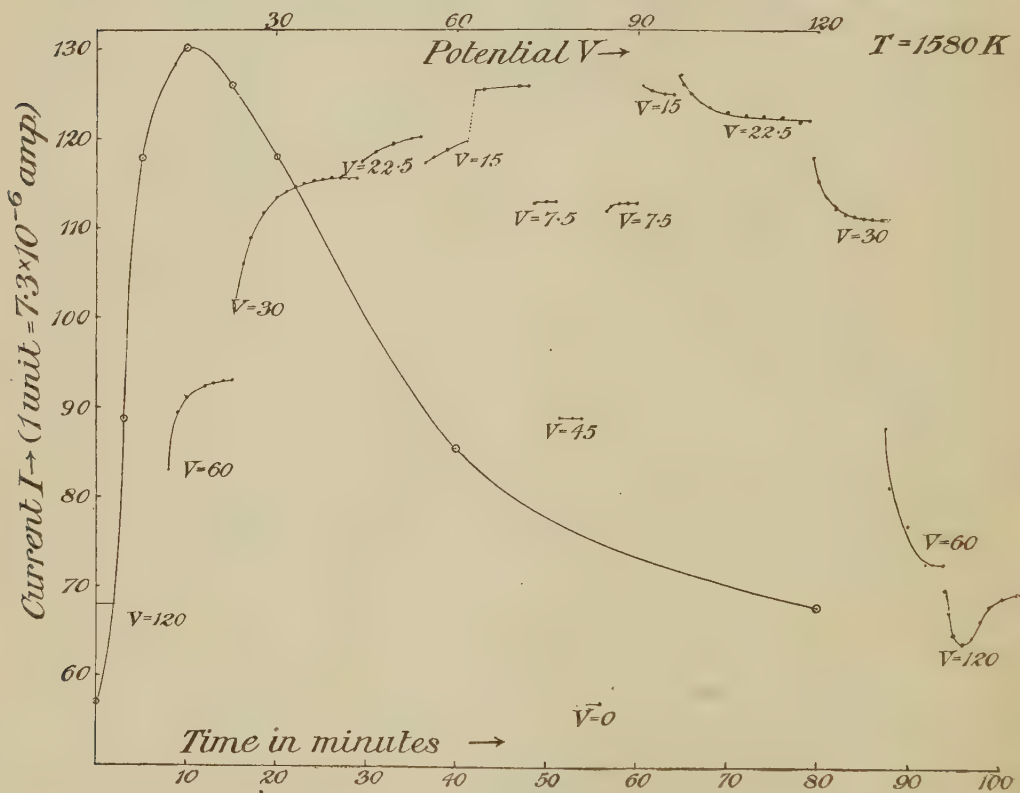


FIG. 14.

eliminate the effect of the previous potential, each potential was taken off for a few minutes before the next was put on. The result (fig. 13) shows the disappearance of the initial drop of the current, but the existence of a maximum value was made very clear.

The same result was obtained with the second filament, which was thicker and perhaps less pure than the first. Although the condition of the vacuum was improved by immersing in liquid air a charcoal tube condenser, which was attached to the filament tube and had been exhausted together with it,

the effect observed was even more striking, as is shown in fig. 14. Two points in the figure deserve special notice. Firstly, the change of the current was so rapid that, in most cases, the initial drop or rising could not be observed. Secondly, there was a shifting of the steady value of the current for the larger potentials. This might be due to the change of the emission during the long interval between the two readings of the current.

The above experiments were made at temperatures of about 1600° K. or more. At such high temperatures the hysteretic effect was more noticeable and persistent. At lower temperatures the existence of the maximum was found to disappear, and the current to decrease after the filament had been strongly heated for some time with a large positive potential on the electrode.

The last series of experiments was concerned with the observance of the occurrence of the maximum current and its corresponding potential at different temperatures. A third tube was used with a filament of the same kind as used in the first tube. The maximum of the current was not so marked as in the previous experiments, but was quite distinct. The potential at which the maximum occurred increases with temperature. At the lowest temperature no maximum was found. The result is shown in the following Table:—

Temperature.	Potential giving maximum current.
1960° K.	60 volts
1720	45
1630	32
1590	28
1480	None.

Taking the maximum value for the current, the relation between the current and the temperature was found to satisfy Prof. Richardson's formula closely,

$$i = AT^{\frac{5}{2}}e^{-b/T},$$

where T is the absolute temperature, A and b are constants, and i is current per unit area of the emitting surface.

Phenomena of the same kind as described above have been noticed before by several investigators on thermionic emission. They were observed first by Prof. Richardson* in his experiments on the emission of positive ions from hot platinum in different gases, by Prof. Richardson and Sheard,† and later by Lester,‡ in experiments on both positive and negative emission of

* 'Phil. Trans.,' A, vol. 207, p. 10 (1906).

† 'Phil. Mag.,' vol. 31, p. 554 (1916).

‡ 'Phil. Mag.,' vol. 31, p. 554 (1916).

hot filaments in vacuum. Langmuir* also found the existence of a maximum current in his experiments on the emission of electrons by tungsten wire in nitrogen, and put forward a theory for its explanation. According to this theory, ionised nitrogen acts upon the hot tungsten, and forms a compound which, though unstable, may remain on the surface of the wire for a short time and while it is on the surface, it is supposed to hinder the emission of the filament. This theory can be extended to account for the effect due to previous potentials on the thermionic current by supposing that the compound on the surface of the filament requires some time to adjust itself to suit new conditions for equilibrium. But, on the other hand, the theory is limited to tungsten in nitrogen, while the same effects have been found to happen with tungsten in an apparently good vacuum, with platinum in a vacuum and in oxygen, in positive as well as in negative emission. The explanation must be of a more general character. But under precisely what conditions the filaments produce such peculiar effects, whether, for instance, it is due to a film formed by chemical action on the filament or otherwise, is not quite clear at present.

In conclusion, the writer wishes to express his thanks to Prof. O. W. Richardson, under whose direction the present research was carried out.

* 'Phys. Rev.,' vol. 2, p. 467 (1913).

The Ultramicroscopic Structure of Soaps.

By W. F. DARKE, J. W. MCBAIN, and C. S. SALMON.

(Communicated by W. B. Hardy, Sec.R.S.—Received November 12, 1920.)

[PLATES 10 AND 11.]

In 1912, Bachmann* published, with Zsigmondy, beautiful pioneer descriptions of the ultramicroscopic appearance and behaviour of soaps. In view of our present greatly extended knowledge of the constitution of soap solutions, sols, gels, and curds, it was highly desirable to extend these morphological observations, and to correlate the various phenomena observed by Zsigmondy and Bachmann with the known constituents of these systems. It was also of great importance to find out to which state, whether sol, gel, or curd, the various phenomena were to be attributed. A further interest lay in the development of the technique of such investigations as, for instance, in the application of the cinematograph to the study of the life-history of an ultramicroscopic particle or formation in its genesis and subsequent transformations.

The present paper contains some novel information with regard to Brownian movement and the distinction between sols, gels, and curds, the three different states which are possible for soaps. Although we have given a year to this work, in each experiment with the ultramicroscope we still find some new detail. We have endeavoured to record only those observations which appear reproducible and characteristic.

States in which Aqueous Soap Solutions exist.

A "soap sol" is to be defined as a clear transparent liquid, whose viscosity may range from that of water up to a value several thousand times as great. Almost invariably there is to be found, floating in these otherwise clear solutions, a sediment of solid soap, the result of the small but definite amount of hydrolysis that is universally exhibited by all aqueous soap systems. Often, again, at lower temperatures, the soap solution deposits the soap which is present in excess of the solubility corresponding to that temperature.

A "soap gel" is a clear transparent body which is identical with a soap sol in every respect, except that it retains a definite form and possesses elasticity. Often a gel is clouded by the formation of a few true curd fibres.

* 'Kolloid-Zeitschr.,' vol. 11, p. 150.

A "soap curd" is a white, more or less opaque, mass. It consists of innumerable curd fibres, enmeshed in which is a soap gel or sol. The concentration of the gel or sol depends upon the temperature and upon the nature of the soap, varying from very high concentration to practically pure water, the latter being the case for the more insoluble sodium soaps of the highest saturated fatty acids.

Finally, in the case of the potassium soaps, there may co-exist with one or more of the above systems transparent tabular crystals of hydrated potassium soap.

The above relationships and types have not hitherto been recognised or described. Their elucidation is primarily the work of Miss M. E. Laing, whose experiments are embodied in a separate communication, amplified by the direct inferences rendered possible by our present observations, and also incidentally corroborated by numerous observations made in this laboratory in connection with other lines of investigation of soaps.

Technique.

Three ultramicroscopes were employed: the Zsigmondy-Siedentopf, the Jentzsch (kindly lent to us by Mr. Emil Hatschek), and the Zeiss Cardioid; the latter with heating appliance.

A heating arrangement was designed and ordered from Zeiss for the Zeiss-Siedentopf microscope shortly before the outbreak of war, but this had not been received. In some of our earlier experiments we employed a home-made cooling bath of ice water, in which the Zsigmondy-Siedentopf cell was immersed. Each form of ultramicroscope possesses serious disadvantages, and it is often necessary to use two forms as check, in order to find out whether observations refer to the inherent structure of the systems under investigation. In the Cardioid form, the whole layer being only 0.001 mm. thick, much of the soap layer lies within the range of influence of the containing silica walls above and below it. The original Siedentopf-Zsigmondy and the Jentzsch forms enable observations to be carried out free from the effects of the containing walls, but no heating arrangement was available, and in many cases it was a matter of great difficulty to retain a given portion or structure of the system under continued observation. Further, visibility was difficult when an opaque layer of soap curd intervened. All final observations were obtained with the Cardioid.

The heating arrangement used with the Cardioid, which consists of a film of platinum on the cover-glass, heated electrically, had to be repaired repeatedly, and the platinum renewed. For this reason the temperatures

are not accurately measured, but they are fixed quite sufficiently for the present purpose by macroscopic observations.

The cinematograph camera was the comparatively inexpensive but satisfactory "Ensign" supplied by Houghton's, Ltd. By marking the position of the driving handle in relation to the shutter, it was possible to take exposures at any required interval from 1/10 second up to several hours. Of course, much of the finer detail, and many observations such as that of Brownian movement of small particles, was beyond the range of any but ocular observations with the highest powers of the ultramicroscope (Zeiss ocular No. 18); Zeiss apochromat N.A. = 0.78 (3 mm.). With the cinematograph and other cameras a Zeiss No. 2 projector was used. Some uncertainty was involved in focussing the cinematograph camera, as this had to be done by focussing on transparent paper in the gate of the machine before mounting the film in the camera. The illumination in all cases was provided by direct current arc taking 30-50 amperes.

Two devices which have been of the greatest assistance are of general application. The first was the insertion of a vertical illuminator, such as is used in metallography, in the tube of the ultramicroscope. By this means an image of the system under investigation is thrown on a screen so that it may be watched during the actual cinematographic or photographic experiment. The second was of service in studying the life history of various particles and fibres during their formation, ageing and disappearance. This was the joining up of the ends of the cinematograph film to make an endless band driven by motor so that it was projected upon the screen before the lantern again and again in rapid succession. The film could be passed backwards or forwards until doubtful points were cleared up.

Brownian Movement and Hydrolysis.

It is of advantage to discuss the Brownian particles first, in order that they may not distract attention from the main interest of the work.

One kind of particle that is almost invariably observed in soap sols, gels and curds is a product of hydrolysis. This type varies in size from particles visible to the naked eye down to those of very low ultramicroscopic dimensions. These particles are in a sense extraneous and an unessential part of the solution, since they are merely a solid product of hydrolysis which is regulated entirely by the low hydroxyl ion concentration in these soap systems.

Brownian movement is exhibited by two other constituents of soap solutions. Thus it is shown by portions of curd fibres which are not attached

to any solid body, such as to a quartz cover-glass or to a network of other fibres.

Much more important are the innumerable milky-white particles which appear to be present in all these soap systems but usually just below the border line of visibility in the highest powers of the ultramicroscope. It is often only when the conditions are exceptionally favourable or in a particularly well illuminated portion of the field that they become just visible; then, however, their existence in immense numbers is undeniable. It is probable that this structural element, like the curd fibres, consists of neutral undissociated soap colloid. In the case of soap solutions that are just above their solidification temperature, sudden cooling serves to develop them into easily visible dimensions. In the case of the higher sodium soaps of the saturated fatty acids, some are often readily visible even above the temperature at which fibres appear, as is more fully described in the discussion below. In a more efficient ultramicroscope they would probably always be visible in all soap systems.

The Brownian movement has been of the greatest assistance in this ultramicroscopic study, since it affords a direct measure of viscosity of the solution and hence very often shows how much soap is still left in the solution. When we know from our experience of soap solutions that the solution itself is highly viscous, Brownian movement is found to be slight or altogether suppressed. The most rapid Brownian movement is attained in soap curds which have stood at room temperature until most of the soap has separated out, leaving only a thin aqueous fluid between the curd fibres. In such cases the larger particles are white, the smallest are purple, and the very rapid motion of the latter is rivalled by the smaller variety of the green particles.

The Brownian particles exhibit two very interesting varieties of movement. The first is when they collect in the surface of a soap-air interface and there carry out Brownian movement in two dimensions, with a vigour depending upon the viscosity of the soap solution in contact with them. Frequently such a surface is crowded with particles.

Another variety of Brownian movement has not been previously described. Very frequently, when a particle has come into contact with a curd fibre, it finds some difficulty in leaving again, although violent activity may still persist in one dimension, namely, up and down the length of the fibre. Sometimes such a particle shakes itself loose.

This peculiar movement, before it was properly understood, led to difficulties in interpreting the nature of various rectilinear spaces and boundaries into which, or out of which, Brownian particles did not seem to be able to move. This was found to be due to the difficulty of crossing the curd fibre which

served as the apparent boundary. In this way sharply defined geometrical figures, occurring as the result of perhaps a chance network of fibres, might easily be mistaken for solid crystals.

Soap Solution and Soap Gels.

Both of these closely similar transparent systems are nearly clear in the ultramicroscope. Except when cooling has developed the neutral colloid into visibility in the form of white particles, the sols and gels usually contain no ultramicroscopic constituents other than a few Brownian particles. The ionic micelle is invisible. Bachmann's paper contains a number of observations with regard to the development of the neutral colloidal particles upon rapid cooling, and he labelled them "first and second solid phases."

The above applies to both potassium and sodium soaps. On the other hand, in the case of the hydrogen soap, cetyl sulphonic acid, the numerous white particles of neutral colloid are always prominent and very numerous; whilst the clear liquid in which they are contained exhibits a fine-grained shimmering activity, as if it were full of movement, although no particles are visible. Possibly this background effect is to be ascribed to the ionic micelle, but more probably it is due to amicroscopic particles of neutral soap.

In the case of sodium oleate gel we made several attempts to find out if any gel structure was visible. The difficulty is to eliminate the presence of the curd fibres. On one occasion a network of fibres was observed, which differed from the curd fibres, also present, in that they were much finer than, and a different colour from, the latter, and also that they had no fine loose ends. These fibres formed one continuous network of curved lines, like expanded sheet metal. When mechanical pressure was applied to one side, so that the whole flowed, this fine network flowed with it, the meshes widening or narrowing, but remaining otherwise intact, whereas the characteristic curd fibres curved and pulled themselves through the gel until they lay in straight lines down the current. This network is probably not the characteristic structure of gels, since the meshes are unexpectedly large, and we have observed gels exhibiting no visible structure. What does seem clear is the tendency towards a filamentous structure, which we believe is probably the general characteristic of soap gels as distinguished from sols. These filaments, however, must normally be amicroscopic.

A few extraordinary fibres were observed in sodium oleate gels. Some resembled a pure sine-wave curve continued with the utmost regularity in a line across the field. Others exhibited similar periodicity, but with numerous harmonics. In every case the surprising characteristic was that any part of one fibre was an exact replica in form and in structure of the corresponding

part of all the other numerous waves of which the fibre was composed. Fig. 1 (Plate 10) is a photograph, obtained with about twenty minutes' exposure, which, however, gives but a faint impression of the remarkable detail observable in these fibres. In appearance the fibre consists of a nearly colourless gelatinous tube, containing white particles of different sizes, shapes and orientation, distributed in rhythmic patterns along the length of the tube. Possibly the curves are produced when the gel shrinks in the direction of the length of the fibres.

SOAP CURDS. FELTS OR PASTES.

1. *Sodium Salts of the Saturated Fatty Acids.*

In this series the laurate, myristate, palmitate and stearate were studied. The distinctive characteristic is that the curds are comprised of a felt of fibres which may be centimetres or inches in length, but which are usually of ultramicroscopic diameter. That is, these curd fibres are dependent upon dark ground illumination for their detection and give only diffraction lines from which their true diameter cannot be inferred. Sometimes the fibres appear to be definitely visible, that is, to be of microscopic diameter; but this is somewhat uncertain since in some cases such fibres can be shown to consist of bundles of parallel ultramicroscopic fibres. The "fibres" which are often visible to the naked eye and which may give the characteristic "feather" to curd soaps are certainly bundles of microscopic or ultramicroscopic fibres.

Surprising as it appears, this is apparently the stable condition of sodium soaps, even after standing for years; although, after this paper was drafted, we discovered that the sediment of the dilute solution of sodium palmitate which had stood for five years consists partly of fibres but partly also of crystals very similar to those of potassium stearate described below. Fig. 2 shows a specimen of this sediment from N/50 sodium palmitate which was introduced into the cardioid cell without warming. Further work will be required to decide whether these crystals are composed of acid or neutral soap and whether they appear within a reasonable time.

If the solution has been kept long enough in contact with glass, definite crystals of silicate are occasionally met with. As will be shown in other communications, the curd fibres exhibit solubility depending upon the temperature, so that they gradually disappear upon warming and are increased on cooling.

Zsigmundy and Bachmann have observed that on ageing the coarser fibres are developed at the expense of the finer ones, as would indeed be expected from consideration of the effects of the surface tension. They also observed

that on ageing the fibrous structure became even more pronounced and exhibited less similarity to crystals or crystallites; this is probably due to the fact that the degree of hydration of the curd fibres has to readjust itself to the altered concentration of the residual mother liquor with which it is in contact. Fresh solutions of soap above the temperature at which fibres appear are not as clear as solutions that have had some time to settle before withdrawing a sample for investigation. This is presumably due to sedimentation of the products of hydrolysis.

(a) *Sodium Laurate* (concentration = 1.0 N).

Above 60° C. this solution is optically clear in the field of the ultramicroscope. On cooling slowly, long thin fibres of characteristic curvature are observed to grow into the field. These fibres appear to increase in length and diameter, and eventually, if the cooling is continued, become so numerous that a felt-like mass is obtained, in which it is no longer possible to distinguish individuals. This behaviour is illustrated in fig. 3. In many cases it appeared as though these fibres had attained their full length before becoming visible, and it seems probable that they must have existed previously, as long chains of molecules or aggregates, below the limit of visibility of the microscope. (This agrees with Zsigmondy and Backmann's impression of the pre-existence of sodium palmitate and stearate and oleate fibres in the optically clear solution.) In no single case were we able to observe the growth of one of these fibres from a nucleus. The fibres are so intertwined as to account for the rigidity of the solid soap. On heating again, the smaller fibres disappear, leaving a coarse network composed only of large fibres, which on further heating do not diminish in diameter, but appear to contract longitudinally from both ends, until they finally disappear, and the liquid becomes optically homogeneous. It was often observed that the shredded ends of these coarse fibres gave the impression that what had appeared to be a single fibre consisted in reality of bundles of fibres.

(b) *Sodium Myristate* (0.75 N).

This soap is very similar in its behaviour to sodium laurate, the fibres being possibly slightly coarser, and in the final state more matted.

(c) *Sodium Palmitate* 1.0 N and 0.25 N.

This solution becomes clear only above 90° C. On cooling, the field usually becomes full of small particles in fairly rapid Brownian movement (sometimes, however, there is only a lightening of the background). As the cooling progresses, the movement becomes less violent, probably owing to

increasing viscosity. At about 75° there is again a rather sudden increase in the number of these particles (*cf.* Zsigmondy and Bachmann). We believe these particles to consist chiefly of neutral colloidal soap. (In 0.25 N solution no such particles were observed.) At 67° thick parallel fibres appear and from this temperature downwards they continue to grow and finally become so numerous that it is no longer possible to distinguish any structure in the dazzling white mass. These fibres are much straighter than laurate fibres, and judging by the amount of diffused light in their neighbourhood they must be of considerable thickness; in fact they can frequently be distinguished even in transmitted light. In 0.25 N solution parallel fibres were obtained by slow cooling; they radiated from definite centres when formed by rapid cooling after insufficient heating. In one particular case, where the specimen had been repeatedly warmed and cooled, and finally allowed to stand for some time, fibres were observed with the naked eye, radiating from a point and which were exactly similar to ordinary crystallites in their appearance. These "crystals" were probably formed as the result of evaporation. This would agree with an earlier observation of McBain and Salmon, where it was noticed that in the evaporation of a concentrated soap solution, at a certain definite concentration, small star-shaped crystals appeared on the sides of the vessel.

(d) *Sodium Stearate* 0.5 N.

This soap is very similar to sodium palmitate, but with the rather remarkable difference that the fibres are frequently "beaded" in appearance (fig. 4). This might be explained by their being crossed by other fine fibres if it were not for their absolute regularity. An alternative explanation is that they possess a spiral structure. This is sometimes supported by the fact that alteration of focus brings into view portions of the fibres which were previously invisible; but it is by no means certain that this is a correct explanation (*cf.* sodium oleate discussed above). It is possible that they may be due to particles held in position by the fibres.

2. *Sodium Salts of the Unsaturated Fatty Acids.*

(a) *Sodium Oleate* 0.6 N.

This solution is of special interest since it can be obtained at room temperature in the three forms, sol, gel, and curd, already described. Under the ultramicroscope the sol appears optically homogeneous. On cooling the curd results, and this appears very much like other sodium soaps, resembling most closely sodium stearate, the corresponding saturated fatty acid. The fibres are beaded in the same manner but to a much greater extent (fig. 5).

(b) *Sodium Rosinate (Abietate).*

The investigation of this specimen appeared to be of great importance in view of its very extensive employment in household soaps. The rosinat investigated was a specimen prepared by Miss K. M. Gibbins, by boiling the best W.W. rosin of commerce with sodium ethylate in dry alcohol. The sodium salt freed from alcohol should, therefore, have contained no appreciable amount of abietic anhydride, and should therefore be comparable with the completely saponified rosin usual in commercial soap.

It was found necessary to use a much more concentrated solution of this thoroughly saponified material than had been indicated by a preliminary experiment with the merely neutralised resin. In order to obtain an appreciable amount of separated rosinat on cooling, it was necessary to make the solution about 3.5 N. At the boiling point this appeared to consist of one liquid phase with a few ultramicroscopic particles in Brownian movement which was very slow on account of the high viscosity of the medium. On cooling, separation into two liquid phases took place, and on further cooling, each of these deposited large amounts of ultramicroscopic particles whose shape could not be directly inferred, except that they appeared decidedly granular, rather than spherical, on account of the asymmetry of the optical changes produced when focus and illumination were altered.

The important point to notice is that there are no fibres but merely irregular granules which have a tendency to arrange themselves into regular lines, like fine grained leather. The behaviour of sodium rosinat is rather like that of a sodium soap whose curd fibres are extremely soluble at the temperature of the experiment. The same explanation may hold for the 0.5 per cent.—1 per cent. gels of sodium palmitate and stearate in alcohol, in which Zsigmondy and Bachmann observed granules only.

Fibres were, however, obtained by the addition of common salt in the concentrated solution just described. In this case, one of the liquid phases continued to deposit granular particles whilst the other developed instead short inconspicuous rather straight fibres, very different from the luminous white fibres of the higher sodium soaps such as palmitate or oleate. The rosinat fibres differ from the other sodium soaps in being only a few hundredths of a millimeter in length, and they differ from potassium fibres in showing no tendency to twin.

3. Potassium Salts of the Saturated Fatty Acids.

The potassium soaps do not form rigid curds like the sodium soaps. Their ultramicroscopic appearance and structure is also quite different. There are

no long curd fibres such as are characteristic of all sodium soaps. Their place is taken by short fibres which are never more than a few hundredths of a millimeter in length. Moreover these short fibres exhibit strong tendency to appear as twins.

Another fundamental difference is the fact that at room temperature, the stable form of potassium soaps is that of true crystals, the fibres being replaced by these small lamellar crystals as Zsigmondy and Bachmann have also clearly shown.

(a) *Potassium Stearate* (0.5 N).

Above 70° this solution is very similar to sodium palmitate, but below this temperature its behaviour depends upon the rate of cooling. We have spent a great deal of time in order to be quite certain that no structural elements are to be found other than those already mentioned. We are, however, satisfied that only three formations ever appear. The first is greatly enlarged Brownian particles of neutral soap, often in violent movement; the second is V-shaped twin crystals or fibres, frequently highly distorted, fig. 6; and the third and permanent form is constituted by the minute lamellar crystals. The appearance of this transition for one particular rate of cooling or ageing has been well shown in the diagrams of Zsigmondy and Bachmann.

At first we were somewhat sceptical with regard to the existence of these crystals, since similar formations are very readily produced by the interlacing of fibres. However, repeated observation of these heaps of crystals during heating shows that they liquefy (possibly to a crystalline liquid) whilst dissolving, and their contours remain smooth and closed even when they are altering and flowing freely. Often in the mass, some of the boundaries appear incomplete.

Very slow cooling gave the clue to the understanding of these systems. Under these circumstances, on cooling below 65° or 70° , only fine sharp twin crystals or fibres form, fig. 7. These steadily grow in length, their diameter remaining apparently rather less than that of sodium curd fibres; with age they become more and more deformed and build up an apparent network structure, which begins to appear in less than an hour after their first formation, fig. 8. On standing for a day or so they begin to be transformed into the stable crystal leaflets, fig. 9, although, like Zsigmondy and Bachmann, we have not been able to observe the actual process, which requires several days at room temperature for completion.

Upon rapid cooling the phenomena take place with such bewildering rapidity, complicated by Brownian movement, that they are much less easy to disentangle. However, it seems clear that the first effect is the rapid

increase in size and numbers of particles of neutral soap, together with agglomerations of these particles, the whole being in movement. Highly distorted, but not recognisable V-shaped fibres and pieces of fibre rapidly appear, fig. 10. These grow, rather slowly, at the expense of the particles of neutral soap. Often a fibre that has been motionless for some time, moves with a jerk across the field and either attaches itself to a fibre or arranges itself with respect to it, until the fibres have become interlaced to form an apparent network which is ultimately replaced by the tubular crystals.

The cloud of larger Brownian particles could be made to appear at any stage of the slow cooling just described, by causing a sudden cooling to take place. It would therefore seem that these fibres possess a true solubility for each temperature, and that sudden lowering of temperature deposits from solution a certain amount of soap, which then redissolves to crystallise out as fibres.

(b) *Phenol and Water.*

Several observations were made with mixtures of phenol and water above and below the critical temperature in order that we might be aware of the ultramicroscopic picture presented by the appearance of a new liquid phase. In every case, no matter how slow or rapid the cooling, numbers of points or round discs of light appear all over the field. This general appearance was wholly different from anything seen in any soap system investigated. A complete description of the phenomena observed in such cases has been published from Zsigmondy's Laboratory by Von Lepkowsky.*

(c) *Potassium Palmitate 1.0 N.*

This soap is identical in its behaviour with the stearate, the twin fibres being perhaps less clearly defined and the final structure less easily resolved.

4. *Hydrogen Soap. Cetyl Sulphonic Acid.*

Cetyl sulphonic acid, $C_{16}H_{31}SO_3H$, is remarkable as being a hydrogen soap and it is of quite special interest because hydrolysis in this case is out of the question.

The microscopic appearance is rather similar to that of potassium soaps, in that innumerable glittering crystals appear to exist in the curd.

A 0.5 N solution prepared as described by Reychler was full of colloidal particles even at temperatures well above that at which curd fibres appeared. The colloidal particles were prominently visible, but in addition the clear intervening liquid exhibited a remarkable shimmering effect as if in intense

* 'Zeitschr. physikal. Chem.,' vol. 75, p. 608 (1911).

fine grained movement. The impression given is that two kinds of colloidal particle are present, one that is readily visible and another which is just upon the border-line of ultramicroscopic visibility but in extremely active Brownian movement. If so, the large particles would be colloidal sulphonic acid, analogous to neutral colloid in soap solutions, and the fine intense movement might just possibly be due to ionic micelle.

On gradual cooling, curd fibres appear. These fibres are short like those of potassium soap, and they also exhibit a tendency to form twins, although in this case the angle of twinning is generally obtuse and the twins are not so well developed. A distinction between these fibres and those of sodium soaps is that they are much finer, so much so that in some cases it would be impossible to detect them were it not for their being overloaded with large Brownian particles like large beads on a thread. Such particles are however in incessant vibration, transverse as well as up and down the thread. Fig. 11 taken on a process plate, exposure 12 seconds, appears somewhat fogged owing to the marked Brownian movement.

Upon standing for some days the fibres show a tendency to develop and aggregate into an apparent network as in the case of potassium soaps. Further, the shimmering appearance is less marked in the dark spaces away from the fibres although quite as pronounced as before in the neighbourhood of the groups of fibres where the Brownian particles tend to assemble.

In further analogy with potassium soaps we have found that tabular crystals appear after standing some days or weeks. These crystals are often very difficult to see on account of their extreme thinness, which of course was much less than $1/1000$ mm. Their crystal form is better developed than in the case of potassium soaps.

Owing to their extreme thinness some of the smaller of these crystals, which are floating in the liquid out of contact with the walls of the cardioid cell, exhibit extraordinary and constant movement. They bend, rotate, and even vibrate transversely with very rapid movement while swimming through the solution. Upon heating, such a moving crystal curls up at both ends, the thickened ends rapidly disappearing; meanwhile the crystal tends to bend spasmodically, forming well-marked obtuse angles in addition to the constantly varying flat curves. The temperature at which the curled-up crystal finally disappears is higher than that at which the fibres vanish; just as in the case of the potassium soaps and in accordance with the predictions of the phase rule for the relative stability of the two phases. Fig. 11 shows such a "crystal" or "liquid crystal" in rapid transverse vibration, and moving freely in the liquid. The photograph distinctly shows very nearly the maximum curvature at a particular instant of vibration.

General Discussion.

Summarising our knowledge of sodium palmitate solutions derived from the work of Chevreul, Krafft, and his co-workers, and papers from this laboratory, especially those of Taylor, Salmon, Laing and Titley, we know that at 0° C. sodium palmitate is very insoluble, separating from solution practically quantitatively in the form of heavily hydrated curd fibres and leaving behind nearly pure water. There is an inappreciable amount of any other colloidal or ultramicroscopic form of soap present in the solution, since, on filtering, practically pure water comes through, and ultramicroscopic observations show clearly that there is only one structural element, namely, these curd fibres.

At 100° C., on the contrary, sodium palmitate is extremely soluble, and although dilute solutions contain crystalloidal matter, concentrated solutions consist chiefly of neutral colloidal sodium palmitate, together with sodium ion and colloidal ionic micelle, which contains part of the neutral colloid. Here practically all the soap is in colloidal form with, say, about one-half of it in the form of neutral colloid. All this colloid, whether neutral soap or ionic micelle, is invisible in the ultramicroscope. Upon gradual cooling, towards 70°, more and more Brownian particles appear. Zsigmondy and Bachmann considered that these were hydrolysed soap. This, however, can hardly be the case since hydrolysis, which has been directly measured, diminishes instead of increasing on cooling. They based this conclusion upon an observation that a small amount of sediment from similar solutions of potassium palmitate and stearate, after "drying," melted at about 100° below the melting point of the pure dry salts. We have shown in an earlier communication that only a part of the water can be removed from soap by drying at 100° *in vacuo*, so that their specimens necessarily contained water. Again, their sediment must have included the small but definite amount of acid soap which does result from hydrolysis, and which is usually present in the form of quite coarse particles. Miss Laing has shown by direct analysis that the curd fibres consist of hydrated neutral soap.

On cooling below 70° the tendency towards definite orientation of the colloid in the sol becomes so pronounced that definite fibres begin to appear. At each temperature there is a definite concentration of soap left behind in solution, the fibres then exhibiting a definite solubility at each temperature. As the temperature is further lowered, more and more fibres separate out. These must be found at the expense of all the other forms of soap in the solution until we arrive at the wet felt of hydrated curd fibres at 0° described above.

This description applies to all the sodium soaps, bearing in mind that the stearate and behenate are more insoluble, and that the oleate, myristate, laurate and rosinate are more soluble, and that the latter contain more crystalloidal matter in their solutions.

This description also applies, in some measure, to the corresponding potassium soaps, remembering that these are more soluble than the sodium soaps, and that the curd fibres are only a few thousandths or hundredths of a millimetre in length, instead of being perhaps many centimetres, and that, finally, upon standing for a short time at room temperature, the soap recrystallises in the form of innumerable thin flat crystals of microscopic dimensions.

It is important to note that we have found that commercial sodium soaps also contain, as sole structural constituent, hydrated curd fibres, with enmeshed liquor, which is a sol or more frequently gel of the various more soluble soaps and salts present.

It is also of great interest to note that in the only case here investigated the fibres of palmitate and rosinate separate out largely independent of each other instead of forming one new kind of mixed fibre. Other direct corroborative evidence will be given in Miss Laing's communication, to which we have several times referred.

Summary.

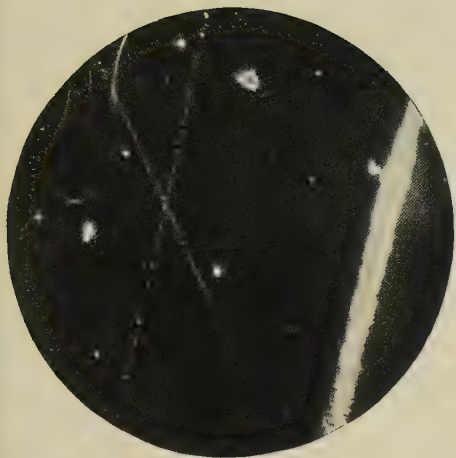
1. The ultramicroscopic observations of Zsigmondy and Bachmann have been confirmed, interpreted and extended. Their observations referred almost entirely to soap curds, not gels or sols, for the latter usually exhibit in the ultramicroscope nothing except Brownian particles, and that only under definite conditions.

2. The cinematograph has been employed as an aid in elucidating the formation and disappearance of the various structures observed.

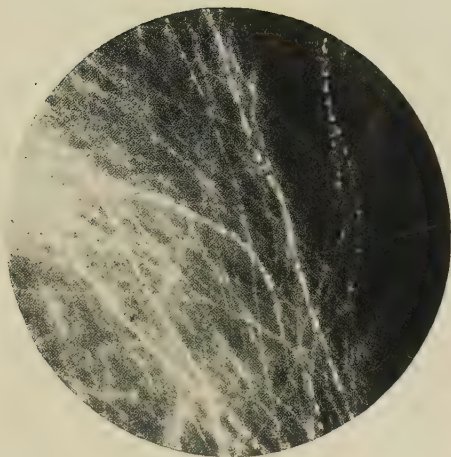
3. Curds of sodium soap consist of a felt of hydrated fibres enmeshing and in equilibrium with a soap sol or gel of definite concentration, the solubility rising rapidly with temperature. The individual fibres may be many centimetres long, but they are barely of microscopic diameter.

4. Potassium soap solutions, on cooling, first develop fibres which are similar to those of the sodium soaps, except that they are only a few hundredths of a millimetre in length, and that they have a strong tendency to form twins. The stable condition at room temperature is, however, the formation of innumerable tiny lamellar crystals of hydrated soap.

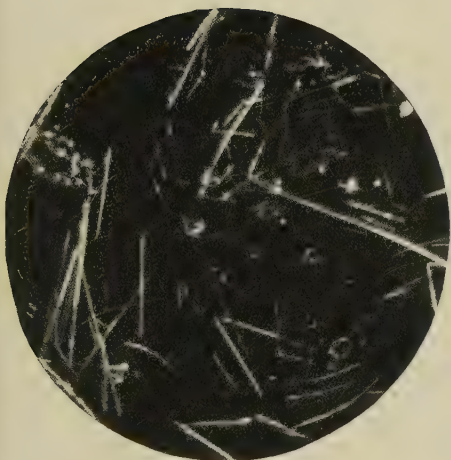
5. The hydrogen soap, cetyl sulphonie acid, is similar to the potassium



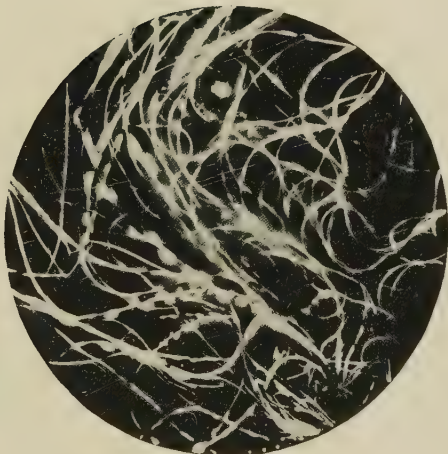
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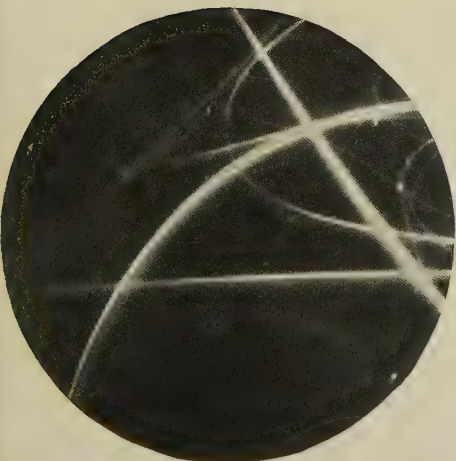
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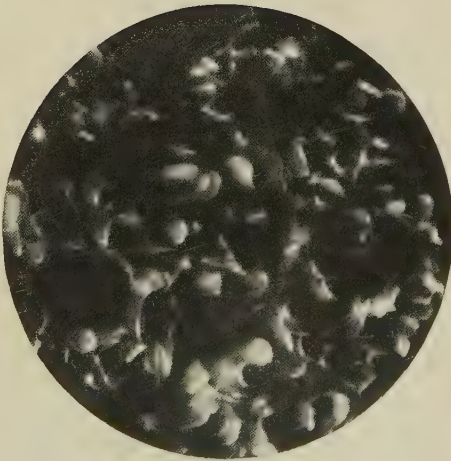
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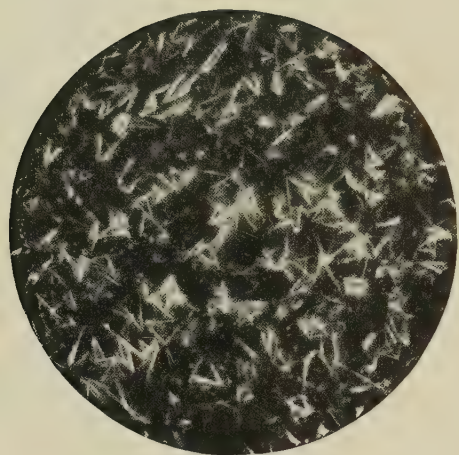
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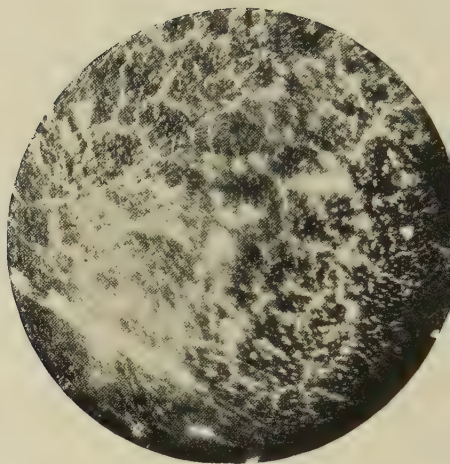
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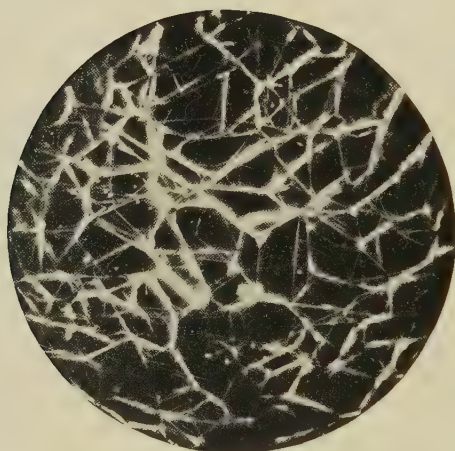
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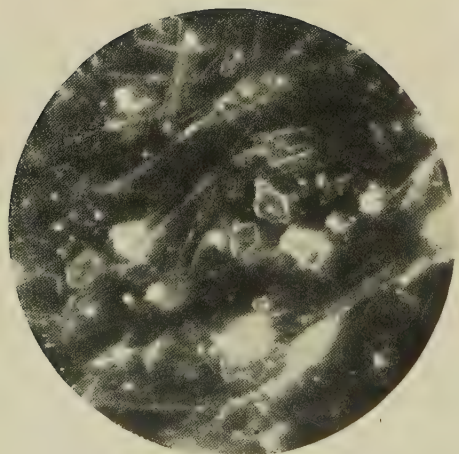
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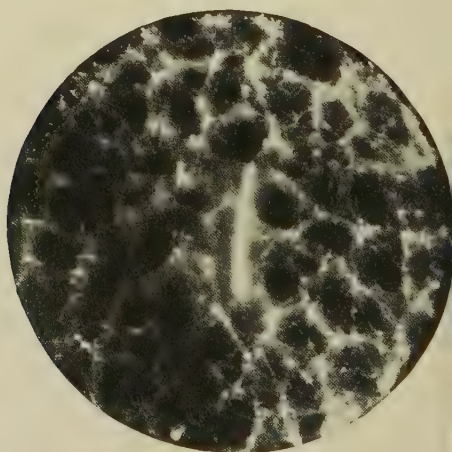
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11

soaps, but the particles of colloidal cetyl sulphonic acid are very much more prominent.

In conclusion, we desire to express our thanks to the Research Fund of the Chemical Society and to the Colston Society of the University of Bristol for grants with which the pure materials were purchased.

DESCRIPTION OF PLATES 10 AND 11.

Figs. 1 and 5, 0.6 N Na oleate ; fig. 2, 0.2 N Na palmitate ; fig. 3, 1.0 N Na laurate ; fig. 4, 0.5 N Na stearate ; figs. 6, 7, 8, and 9, 0.5 N K stearate ; figs. 10 and 11, 0.5 N cetyl sulphonic acid. Figs. 2-11 refer to curds. Magnification $\times 500$ in figs. 1, 2, 5, 7, 8, and 11 ; $\times 600$ in figs. 3, 4, 6, 9, and 10.

The Transmission of Electric Waves around the Earth's Surface.

By H. M. MACDONALD, F.R.S.

(Received January 10, 1921.)

In the 'Proceedings,'* Prof. G. N. Watson discusses the effect of a perfectly conducting layer in the atmosphere at a uniform height above the earth's surface on the transmission of electric waves round the earth. The mathematical treatment adopted by him assumes that the time factor $e^{-\alpha C t}$ can be removed from all the equations, and that the analytical results thus obtained represent the effect of a simple oscillator placed near the earth's surface. The assumption that the time factor can be removed is equivalent to assuming that a steady state of oscillations exists in the space between the two spheres, such that at the end of a period the amplitudes of the electric and magnetic forces are identical at each point with the values they had at the beginning of the period. Now, when the surfaces of both spheres are perfectly conducting, no energy is transmitted across either surface, and therefore, if there is a steady state of oscillations in the space, the total energy in the space must be constant. When there is an oscillator in the space emitting electric waves, there is a finite amount of energy radiated from the oscillator in each period, and therefore the total energy in the space does not remain constant ; it follows that in such a case there is no steady state of

* 'Roy. Soc. Proc., A, vol. 95, p. 546.

oscillations and the mathematical problem involved cannot be treated by assuming that there is a time factor which can be removed.

The effect of any electric disturbance set up in the space between the two perfectly conducting spherical surfaces can be expressed in the usual way in terms of the natural periods of the space. If a and b are the radii of the two concentric spherical surfaces, the equation which determines the periods corresponding to the Legendre function of order n , when the disturbance is such that the lines of magnetic force are circles with the axis of the harmonics as a common axis, is

$$\frac{d}{da} \{a^{\frac{1}{2}} J_{n+\frac{1}{2}}(\kappa a)\} \frac{d}{db} \{a^{\frac{1}{2}} K_{n+\frac{1}{2}}(\kappa b)\} - \frac{d}{db} \{b^{\frac{1}{2}} J_{n+\frac{1}{2}}(\kappa b)\} \frac{d}{da} \{a^{\frac{1}{2}} K_{n+\frac{1}{2}}(\kappa a)\} = 0, \quad (1)$$

where κV is the frequency.* When the disturbance consists of a single pulse at a point near the surface of the inner sphere for which $\theta = 0$, it can be shown that the value of γ , the magnetic force at any time, is given by the relation

$$\begin{aligned} \psi &= \gamma r \sin \theta = A \sum_{n=1}^{\infty} \sum_{\kappa} (n + \tfrac{1}{2}) (v u_a' - u v_a') \\ &\quad (1 - \mu^2) \frac{dP_n}{d\mu} \cos \kappa V t \left/ [a \{1 - n(n+1)/\kappa^2 a^2\} - b \{1 - n(n+1)/\kappa^2 b^2\} (v_a'/v_b')^2] \right. \\ &+ B \sum_{n=1}^{\infty} \sum_{\kappa} (n + \tfrac{1}{2}) (v u_a' - u v_a') \\ &\quad (1 - \mu^2) \frac{dP_n}{d\mu} \sin \kappa V t \left/ [\kappa a \{1 - n(n+1)/\kappa^2 a^2\} - \kappa b \{1 - n(n+1)/\kappa^2 b^2\} (v_a'/v_b')^2] \right., \end{aligned} \quad (2)$$

where $v = (-)^n (\pi/2)^{\frac{1}{2}} (\kappa r)^{\frac{1}{2}} J_{-n-\frac{1}{2}}(\kappa r)$, $u = (\pi/2)^{\frac{1}{2}} (\kappa r)^{\frac{1}{2}} J_{n+\frac{1}{2}}(\kappa r)$, and the summation with respect to κ extends to all the values of κ that satisfy equation (1), that is the equation

$$v_b' u_a' - v_a' u_b' = 0. \quad (1')$$

The effect due to any symmetrical disturbance can be deduced from the relation (2).

When the inner sphere is imperfectly conducting, or when the space outside the outer sphere is imperfectly conducting, or both are imperfectly conducting, a similar, though necessarily somewhat more complicated, analysis applies. For example, when the inner sphere is imperfectly conducting, the outer surface, radius b , being perfectly conducting, the equation which deter-

* Cf. J. J. Thomson, 'Recent Researches in Electricity and Magnetism,' § 315 (1893)

mines the frequencies and rates of decay corresponding to the Legendre function of order n is

$$\begin{aligned} \frac{\partial}{\partial a} \{a^{\frac{1}{2}} J_{n+\frac{1}{2}}(\kappa a)\} \frac{\partial}{\partial b} \{b^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota \kappa b)\} - \frac{\partial}{\partial a} \{a^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota \kappa a)\} \frac{\partial}{\partial b} \{b^{\frac{1}{2}} J_{n+\frac{1}{2}}(\kappa b)\} \\ = \frac{\iota \kappa \sigma}{4\pi V} \left[J_{n+\frac{1}{2}}(\kappa a) \frac{\partial}{\partial b} \{b^{\frac{1}{2}} K_{n+\frac{1}{2}}(\iota \kappa b)\} - K_{n+\frac{1}{2}}(\iota \kappa a) \frac{\partial}{\partial b} \{b^{\frac{1}{2}} J_{n+\frac{1}{2}}(\kappa b)\} \right] \\ \frac{\partial}{\partial a} \{a^{\frac{1}{2}} J_{n+\frac{1}{2}}(\kappa' a)\} \Big/ J_{n+\frac{1}{2}}(\kappa' a), \end{aligned}$$

where $\kappa'^2 = -4\pi\iota\kappa V/\sigma$, and the values of κ are complex quantities. It can be readily shown that when the conductivity of the inner sphere is of the same order as the conductivity of sea-water, the rates of decay associated with the frequencies that are of the order of those of the waves of wireless telegraphy are small when $b-a$ is small compared with b ; it follows that the time required to establish an approximately steady state is impracticably long.*

A Comparison of Magnetic Declination Changes at British Observatories.

By C. CHREE, Sc.D., LL.D., F.R.S.

(Received January 27, 1921.)

In spite of the very varied use of the compass needle for purposes of navigation and surveying, there is little really known about the closeness in the parallelism of daily magnetic changes in different parts of the United Kingdom. The mean annual values from magnetic observatories show that, since 1910, secular change of declination has been at least approximately the same throughout England, the south of Scotland, and the south-west of Ireland. Thus the conditions have been favourable for an enquiry into the parallelism of other changes.

Diurnal inequalities from five selected quiet days a month were published for Falmouth as well as Kew up to 1912. A comparison of results from a number of years combined had shown little difference between the diurnal inequalities at the two stations as regards the range. Difference in local

* The rates of decay of electrical currents in an imperfectly conducting sphere have been investigated by Prof. H. Lamb, "Electrical Motions in Spherical Conductors," 'Phil. Trans.,' Part II, p. 530 (1883).

time produced a visible effect, but it was small. In more recent years, corresponding diurnal inequalities for Eskdalemuir and Kew from the five international quiet days of each month had shown a close similarity.

On the other hand, it had been found that, while a regular diurnal inequality of declination is derivable from a number of disturbed days combined, it differs markedly in type as well as in range from the quiet day inequality; also, comparisons of Kew and Eskdalemuir disturbed curves had shown a marked tendency for the latter to be the more disturbed station.

Various lines of investigation have been followed. A comparison has been made of diurnal inequalities at Eskdalemuir and Kew, based on days of different magnetic character, varying from the international quiet days of 1913-16 to groups of days respectively of characters 0 (quiet), 1 and 2 (highly disturbed) during several months of 1919, when a declination magnetograph was in operation at Eskdalemuir. The difference between the Eskdalemuir and Kew diurnal inequalities was found to increase with the amount of disturbance, and to be of the same general type as the difference between disturbed days' and quiet days' inequalities at Kew.

Next, an attempt was made to see how closely mean daily and mean hourly values at Kew and Eskdalemuir agreed when a constant correction was applied to the Kew value, representing the mean difference of declination at the two places. All such comparisons are necessarily affected by any base value uncertainty at either station.

The Eskdalemuir value being calculated from the Kew value in the way indicated above, the calculated mean for the average day of the several months considered was found to differ from that actually observed by about 0.5'. Any error in the assumed base line values would be likely to exaggerate this difference.

The variability in the case of the hourly values was measured by the range in the quantity D (declination) at Eskdalemuir— D at Kew, derived from the mean values for each of the twenty-four hours of the day. It was found to depend greatly on whether the day was quiet or disturbed, the mean ranges obtained being 2.1' for character 0, 3.2' for character 1, and 7.6' for character 2 days. The months considered contained no disturbance of the first order, but on one day of character 2 the observed range in D at Eskdalemuir— D at Kew was no less than 32.9'. We may regard the half of the mean range as representing the worst mistake likely to be made on the average day of the magnetic character considered, in arriving at the declination appropriate to a field station in the south of Scotland from observations extending over an hour, when the reduction to the mean value for the day is dependent on magnetograms taken in the south of England.

When the observations in the field are limited, as is usually the case, to a few minutes, the uncertainty is naturally greater. But, even if such were not the case, it is obvious that, for high accuracy, field observations taken on days of character 2 had better be scrapped.

Oscillations of considerable size sometimes occur on days the greater part of which is very quiet, and they are often numerous on days when there is no very large range of declination. In a previous paper* dealing with Eskdalemuir (E), Stonyhurst (S), Falmouth (F), and Kew (K) curves for a good many months of 1908-9, I had found for the mean values of the ratios of the oscillation amplitudes

$$E/K = 2.14; S/K = 1.68; F/K = 1.14.$$

The ratios derived from different oscillations, or even from the mean oscillation of a single day, showed a considerable range of values, but so marked was the pre-eminence of the Eskdalemuir and Stonyhurst oscillations that there was no single case in which the amplitude at Kew exceeded that at Eskdalemuir, and in only 1 out of 533 cases was the amplitude larger at Kew than at Stonyhurst.

This comparison was repeated for disturbances from June to December, 1919, at Eskdalemuir, Stonyhurst, and Kew, but with very different results. As before, there was no single day which gave a lower mean amplitude at Eskdalemuir than at Kew; but the mean value of E/K from 295 oscillations was only 1.54, the values of the ratio for individual days varying from 1.21 to 2.09.

There was an even larger reduction in the mean value of S/K , which was only 1.01. Also, while October gave a mean value of 1.16, the value falling below unity in only 2 out of 16 days, the months of July, August, and September combined gave a mean of only 0.89, and on only 1 out of 25 days did the ratio exceed unity.

In view of these unexpected results, a comparison was instituted between oscillations at Kew and at Falmouth, extending from January, 1908, to May, 1913, when registration ceased at Falmouth. In all, 2441 declination oscillations, occurring on 489 days, were measured. The mean value of F/K exceeded unity in 45 out of the 49 months from January, 1908, to January, 1912, the mean from the four complete years, 1908 to 1911, being 1.16. But the mean for 1912 was only 1.00, and only one month, from February, 1912, to April, 1913, gave a value in excess of 1.

It is clear that, whilst the ratio of the amplitudes of declination oscillations at two stations in the United Kingdom may show a marked approach

* 'Inst. of Electrical Engineers,' vol. 57, p. 591.

to constancy for months at a time, it may show large variations over a period of years. It is largely dependent on circumstances other than the geographical co-ordinates of the stations. For a complete elucidation of the phenomena much further investigation is required, in which account must be taken of all the magnetic elements.

In the present enquiry the author is much indebted to the kind co-operation of the Rev. A. L. Cortie, S.J., and Dr. Crichton Mitchell, F.R.S.E. The former lent a number of Stonyhurst curves, while the latter supplied the Eskdalemuir curves with full particulars of the hourly values and base-line values.

A more complete discussion, with full particulars of the observational data, will be published in the 'Geophysical Memoirs' of the Meteorological Office.

Siren Harmonics and a Pure Tone Siren.

By E. A. MILNE and R. H. FOWLER.

(Communicated by Prof. A. V. Hill, F.R.S. Received November 9, 1920.)

§ 1. *Introduction.*—This paper deals with the purity of tone of the sound produced by an ordinary Seebeck siren, and with the problem of designing a siren to produce a pure, or comparatively pure, tone. The results were obtained in the course of certain technical experiments on the location of aircraft by sound: they seem, however, to be of more general interest, as a source of sound giving a fairly pure tone of some intensity, whose frequency may be varied at will, is not easily obtainable. The results here described were obtained by the authors in the course of their work as technical officers of the Munitions Inventions Department, and are published by permission of the Department. The experiments were carried out at the Acoustical Research Section of the Department with the help of Major W. S. Tucker, R.E. The authors' best thanks are due to Major Tucker and his staff for their assistance.

The Seebeck siren, as described in books on sound, consists essentially of a revolving disc bored with holes, against which a stream of air is driven from a delivery pipe. The holes are equally spaced round a circle, and the pipe is fixed so that as the disc revolves the holes pass the mouth of the pipe in succession; when no hole is opposite the pipe the flow of air is partially or completely interrupted, and as a hole approaches and passes the flow of air waxes and wanes. When the disc is rotated sufficiently fast, a musical note

is produced, whose frequency is equal to the number of holes passing the pipe per second.

In general, however, the note thus generated is not a pure tone, for the disturbance in the flow of air, though periodic, is not exactly simple harmonic. If the disturbance is represented by a Fourier's series, the series will contain more than one term, and the later terms must give rise to tones which are harmonics of the fundamental tone. Now a siren is a convenient source of sound when a note is required whose frequency may be varied at will, but in such cases the purity of tone may also be important. It is therefore of some importance to examine the relative intensities of the fundamental tone and its harmonics in ordinary cases. The present paper briefly investigates this matter. A theory is constructed which allows an approximate calculation of the relative intensities to be made in any given case. These calculations were carried out for an ordinary siren with circular holes and a pipe with an equal circular mouth, giving a strong first harmonic, and the results were compared with an experimental determination. The approximate truth of the theory was confirmed by the agreement of the observed and calculated ratios.

The theory, if strictly true, showed how a siren could be designed to give a pure tone by suitably modifying the shapes of the mouth of the pipe and the holes in the siren disc. Such a siren was made and tested, and found satisfactory. Though the first harmonic was still perceptible, its intensity was markedly reduced and the intensity of the higher harmonics was quite small. Of the total energy leaving the siren in the form of regular sound waves, about 95 per cent. appeared, in one set of experiments, to be possessed by the fundamental tone in the case of the new siren, for fundamental frequencies of about 350. The *theoretical* maximum percentage possible for any siren with circular holes is 82 per cent. Even for frequencies as low as 100 the octave in the new siren was seven times as weak as in the Seebeck siren used in the experiments.

We describe the theory, and our scanty experimental tests of it, in §§ 2-4, and then describe the construction of our pure tone siren in § 5. The required form of the holes in the siren plate is shown in fig. 5, and its purity of tone in figs. 3 and 6; fig. 3 providing a direct comparison with the Seebeck siren.

Since these results were obtained (1918), Major Tucker has done further experiments with the new siren, under somewhat different conditions. He has kindly provided us with the curves of fig. 7, which confirm the superiority of the new siren. His results for the Seebeck siren, however, do not seem to fit in with our theory of siren harmonics. This discordance

may be only apparent, but much more exhaustive experiments are required than wartime conditions allowed before the proper value of this theory can be determined.

§ 2. *General Theory of Siren Harmonics.*—The sound waves originate from the region of the orifice of the air supply pipe, which at appreciable distances may be considered as a point source. The flux of air from this source is variable with the time: it may be regarded as a steady stream with superimposed oscillations. It is with these oscillations that we have to deal. The siren mechanism, in effect, is merely an apparatus for varying the total area of the orifice of the supply pipe, and it seems plausible to assume that *the actual flux of air at any moment is proportional to the area of the orifice exposed*. This must be very nearly true, whether the pipe abuts closely on the disc, or whether there is appreciable clearance between the pipe and disc, assuming a supply of air at constant pressure.

Waiving the special geometrical conditions of the problem, we may liken the siren to an isolated source in three dimensions, giving rise to a diverging series of waves, with a velocity potential, ϕ , given by

$$\phi = \frac{f(t-r/c)}{4\pi r},$$

where t is the time, r the distance from the source, and c the velocity of sound. The actual flux at the source is (omitting a density factor)

$$\lim_{r \rightarrow 0} \left(-4\pi r^2 \frac{\partial \phi}{\partial r} \right) = f(t).$$

Thus, on our own assumption, the function $f(t)$ must be taken to be proportional to the area of orifice exposed at time t .

Let this function be expressed in (say) a cosine series

$$f(t) = A_0 + A_1 \cos 2\pi p t + \dots + A_n \cos 2\pi p n t + \dots,$$

where p is the fundamental frequency, obtained from a revolution counter on the siren. Now, the radial velocity of the air at distance r at time t is given by

$$-\frac{\partial \phi}{\partial r} = \frac{f(t-r/c)}{4\pi r^2} + \frac{f'(t-r/c)}{4\pi r c}.$$

For values of r , large compared to the wave-length of the fundamental, the first of these terms may be neglected; on substituting the cosine series, the velocity is found to be

$$-\frac{p}{2rc} \sum_n A_n \sin 2\pi p n (t-r/c),$$

and the energy associated with the n th harmonic (*i.e.*, the intensity of the n th harmonic) is seen to be proportional to $n^2 A_n^2$. This result must apply to the siren source.

§ 3. *Harmonics of the Circular-hole Siren.*—As a typical example of ordinary siren apparatus, we will apply the foregoing to the case of a series of equally spaced *circular* holes and an air-delivery pipe, also circular in section and of the same diameter as the holes. For convenience we will neglect the curvature of the circle along which the holes are placed and suppose them to be in a straight line. We must first determine the Fourier series, expressing the area common to one of the holes and a section of the pipe in any position. The lower half of fig. 1 shows the graph of this area

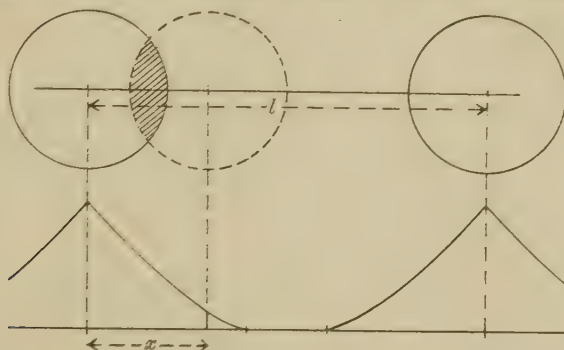


FIG. 1.—Siren holes and overlapping orifice, with the corresponding graph of $A(x)$.

plotted against the position of the centre of the pipe; it is at once apparent that some at least of the early harmonics must be appreciable, from the notable departure of the graph from a sine curve.

Let a be the diameter of a hole, l the distance between the centres of adjacent holes. We shall suppose first that $l \geq 2a$, so that the orifice never covers portions of two holes simultaneously. Let $A(x)$ be the area common to the pipe and a hole, when the centre of the pipe is displaced a distance x from the centre of some particular hole. Clearly $A(x)$ is an even function of x , with period l ; thus

$$A(x) = A(-x) = A(l-x), \quad (1)$$

and further

$$A(x) = 0, \quad (a \leq x \leq l-a). \quad (1')$$

The function $A(x)$ may be expanded in a Fourier's cosine series in the form

$$A(x) = \frac{1}{2}a_0 + \sum_{n=1}^{\infty} a_n \cos 2\pi nx/l, \quad (2)$$

where the coefficients will be given by

$$\begin{aligned} a_n &= \frac{2}{l} \int_0^l A(x) \cos \frac{2\pi nx}{l} dx \\ &= \frac{4}{l} \int_0^a A(x) \cos \frac{2\pi nx}{l} dx, \end{aligned} \quad (3)$$

in virtue of (1) and (1'). Integrating (3) by parts, and noting that $A(x) = 0$ when $x = a$, we have for $n \geq 1$

$$a_n = -\frac{2}{\pi n} \int_0^a \sin \frac{2\pi n x}{l} \frac{dA(x)}{dx} dx.$$

But it is easily seen geometrically that

$$dA(x) = -2\left(\frac{1}{4}a^2 - \frac{1}{4}x^2\right)^{\frac{1}{2}} dx,$$

and hence

$$\begin{aligned} a_n &= \frac{2}{\pi n} \int_0^a \sin \frac{2\pi n x}{l} (a^2 - x^2)^{\frac{1}{2}} dx, \\ &= \frac{4a^3}{l} \frac{1}{z} \int_0^1 \sin zt (1-t^2)^{\frac{1}{2}} dt, \end{aligned} \quad (4)$$

where

$$z = 2\pi n a / l. \quad (5)$$

The coefficients a_n have thus been shown to depend simply on the function $S(z)$, defined by the equation*

$$S(z) = \frac{1}{z} \int_0^1 \sin zt (1-t^2)^{\frac{1}{2}} dt. \quad (6)$$

If we expand the sine and integrate term by term, we obtain, after reduction,

$$S(z) = \frac{\pi}{8} \sum_0^{\infty} \frac{(-)^n \left(\frac{1}{2}z\right)^{2n}}{\Gamma(n + \frac{3}{2}) \Gamma(n + \frac{5}{2})}; \quad (7)$$

this series, when written out in full, takes the form

$$S(z) = \frac{1}{1^2 \cdot 3} - \frac{z^2}{1^2 \cdot 3^2 \cdot 5} + \frac{z^4}{1^2 \cdot 3^2 \cdot 5^2 \cdot 7}, \quad (8)$$

which converges for all values of z , and may be used for computation if z is not too large.

When $|z|$ is large, we can obtain an asymptotic expansion for $S(z)$ by constructing contour integrals of Barnes' type† for the series (7), and transforming these in the usual way. We can thus obtain, when $|\operatorname{am} z| < \pi$,

$$S(z) - \frac{\pi}{2z^2} Y^1(z) \sim \frac{1}{z^2} + \frac{1}{z^4} - \frac{1^2 \cdot 3}{z^6} + \frac{1^2 \cdot 3^2 \cdot 5}{z^8} - , \quad (9)$$

* This function is closely allied to Bessel's functions of order unity. It is a particular case of Lommel's function (Nielsen, 'Handbuch der Zylinderfunctionen,' p. 54), denoted in Nielsen's notation by

$$\frac{3^2}{\pi \cdot z^2} Z^1(z).$$

The properties of the function contained in equations (7), (8) and (9), which we require here, can be deduced from formulæ given by Nielsen, *loc. cit.*, pp. 54 and 228, or more simply obtained directly as indicated in the text.

† Whittaker and Watson, 'Modern Analysis,' 2nd ed., pp. 280, 337.

where $Y^1(z)$ is Neumann's second solution of Bessel's equation of order unity, as defined by Nielsen.* The asymptotic form of $Y^1(z)$ is well known,† and equation (9) is suitable for numerical work when $|z| \geq 8$. The complete expansion is

$$S(z) \sim \frac{1}{z^2} + \frac{1}{z^4} - \frac{1^2 \cdot 3}{z^6} + \frac{1^2 \cdot 3^2 \cdot 5}{z^8} - \dots$$

$$+ \frac{1}{z^2} \left(\frac{\pi}{2z} \right)^{\frac{1}{2}} \left[\cos \left(z - \frac{1}{4} \pi \right) \left\{ -1 - \frac{1^2 \cdot 3 \cdot 5}{(8z)^2 2!} + \frac{1^2 \cdot 3^2 \cdot 5^2 \cdot 7 \cdot 9}{(8z)^4 4!} - \dots \right\} \right.$$

$$\left. + \sin \left(z - \frac{1}{4} \pi \right) \left\{ \frac{1 \cdot 3}{(8z) 1!} - \frac{1^2 \cdot 3^2 \cdot 5 \cdot 7}{(8z)^3 3!} + \dots \right\} \right].$$

The following short Table has been calculated by means of (8) and (9): fig. 2 exhibits the variation of $S(z)$ as a graph.

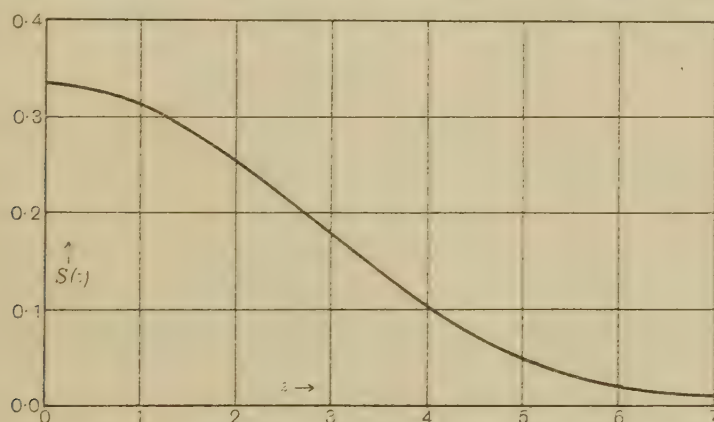


FIG. 2.—Graph of the function $S(z)$.

Table I.

z .	$S(z)$.	z .	$S(z)$.
0	0.3333	4.5	0.0749
0.5	0.3278	5	0.0508
1	0.3117	6	0.0209
1.5	0.2864	7	0.0111
2	0.2540	8	0.0120
2.5	0.2169	9	0.01451
3	0.1780	10	0.01401
3.5	0.1400	12	0.00647
4	0.1050		

* *Loc. cit.*, p. 11.

† Nielsen, *loc. cit.*, p. 156. Tables, from which the values of $Y^1(z)$ may be obtained, are given in 'Rep. Brit. Ass.,' 1913, p. 115.

If $\frac{1}{2}l \leq a \leq l$, so that in certain positions the orifice covers portions of two holes simultaneously, the total area covered is seen to be

$$\begin{aligned} A(x), & \quad (0 \leq x \leq l-a); \\ A(x) + A(l-x), & \quad (l-a \leq x \leq \frac{1}{2}l); \end{aligned}$$

where $A(x)$ is as above. The coefficients a_n are now given by

$$\begin{aligned} a_n &= \frac{4}{l} \left(\int_0^{l-a} A(x) + \int_{l-a}^{\frac{1}{2}l} \{A(x) + A(l-x)\} \right) \cos \frac{2\pi nx}{l} dx \\ &= \frac{4}{l} \int_0^a A(x) \cos \frac{2\pi nx}{l} dx, \end{aligned}$$

which is the same as before. Thus, combining the two cases, we see (on evaluating a_0) that for $0 \leq a \leq l$ the effective area of the orifice is represented by the series

$$\frac{4a^3}{l} \left[\frac{1}{6} + \sum_{n=1}^{\infty} S \left(\frac{2\pi na}{l} \right) \cos \frac{2\pi nx}{l} \right], \quad (10)$$

and the intensities of the harmonics are proportional to

$$\{n S(2\pi na/l)\}^2. \quad (11)$$

The following Table shows the ratios of the intensities of the early harmonics for various values of a/l . To afford some indication of the applicability of this Table, it may be mentioned that the siren used in the tests of § 4 was provided with three alternative rings of holes comprising 4, 8, 16 holes respectively, the rings having radii of 4, 5, 6 inches respectively and the holes being $\frac{1}{2}$ inch in diameter. For a set of q holes spaced round a circle of radius r , $l = 2\pi r/q$ and $2\pi a/l = aq/r$; the values of this ratio for the three sets of holes mentioned are $\frac{1}{2}$, $\frac{4}{5}$, $\frac{4}{3}$ respectively, corresponding roughly to the first three rows in the Table.

Table II.—Relative Intensities of Harmonics for Circular-hole Sirens (Calculated).

$2\pi a/l$.	a/l .	Fundamental ($n = 1$).	Octave ($n = 2$).	Twelfth ($n = 3$).	3rd harmonic ($n = 4$).	4th harmonic ($n = 5$).
0·5	0·08	1·00	3·62	6·88	9·62	10·9
1	0·16	1·00	2·66	2·94	1·82	0·66
1·5	0·24	1·00	1·55	0·62	0·086	0·040
2	0·32	1·00	0·68	0·067	0·036	0·076
3	0·48	1·00	0·055	0·060	0·021	—
4	0·64	1·00	0·052	0·034	—	—
5	0·80	1·00	0·304	—	—	—
6	0·96	1·00	0·384	—	—	—

It is at once apparent that for small values of a/l only a small fraction of the total energy is concentrated in the fundamental, which is indeed considerably less intense than the harmonics immediately succeeding it. It appears further (the same thing is suggested by mere inspection of the curve of $S(z)$) that as a/l increases the relative prominence of the fundamental increases, and attains a maximum when $2\pi a/l$ is about 3 or 4, or a/l about 0.5; at this maximum the first harmonic contains only about 5 per cent. of the energy of the fundamental. To compare the energy in the fundamental with the total energy, we may proceed as follows: Differentiate (10) to obtain the series for $dA(x)/dx$ and apply the well-known theorem concerning the sums of the squares of the coefficients in a Fourier series. We find, for $0 \leq a \leq \frac{1}{2}l$,

$$\frac{l}{2} \cdot \left(\frac{8\pi a^3}{l^2} \right)^2 \sum_1^\infty n^2 \left[S \left(\frac{2\pi na}{l} \right) \right]^2 = \int_0^l \left(\frac{dA(x)}{dx} \right)^2 dx = 2 \int_0^a (a^2 - x^2) dx = 4a^3/3,$$

or, putting $2\pi a/l = y$,

$$\frac{\pi}{3y^3} = \sum_1^\infty n^2 [S(ny)]^2 \quad (0 < y \leq \pi), \quad (12)$$

so that the fraction of the energy concentrated in the fundamental is

$$\frac{[S(y)]^2}{\sum_1^\infty [nS(ny)]^2} = \frac{3y^3}{\pi} [S(y)]^2.$$

The following Table shows the value of this fraction for various values of y or $2\pi a/l$:—

Table III.

$2\pi a/l$.	$\frac{1}{2}$.	1.	$1\frac{1}{2}$.	2.	3.
Fraction	0.013	0.093	0.265	0.493	0.818

Thus for $2\pi a/l = 3$, or $a/l = 0.48$, 82 per cent. of the energy occurs in the fundamental, and the tone is fairly pure. For the extended range $\frac{1}{2}l < a \leq l$, the expression for the sum of the series in (11) is somewhat complicated, and we shall not pause to evaluate it. It seems probable, however, that the best approximation to a pure tone is obtained for values of a/l in the neighbourhood of 0.5.

§ 4. *Experimental Verification.*—It must be remembered that aural estimates of the relative intensities of sounds do not agree with the calculated intensities; the “loudness” of a note is more nearly proportional to the amplitude of an oscillation than to its square. The actual intrusion of the

octave, twelfth, etc., will, therefore, not be so pronounced as the Table would appear to show; but it is not difficult to detect them with the naked ear.

A series of numerical tests were carried out in conjunction with Major Tucker, using his hot-wire microphone.* The microphone was mounted in the orifice of a Helmholtz resonator placed near the siren, and connected with an amplifier, rectifier, and galvanometer. The evidence available at the time of these experiments showed that the galvanometer deflection was proportional to the *energy* of the resonant vibrations of the air in the resonator. The resonator has a single free period (in general) and does not respond to the octave of its own particular note. The siren was run at a series of speeds, and the deflection read for each speed. If the siren note is pure, the curve of deflection against speed should show a single peak, the abscissa of which must correspond to the note of the resonator; the presence of other peaks indicates that the frequency corresponding to the resonator is a constituent of the siren note for other speeds of rotation.

The dotted curve in fig. 3 is such a curve, though on this occasion the

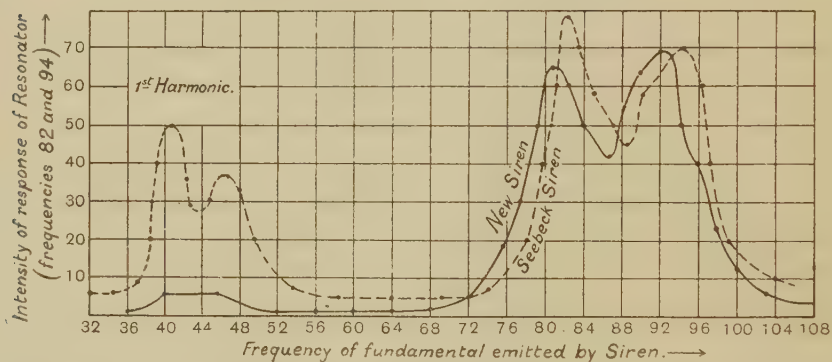


FIG. 3.—Comparative test of purity of notes emitted by Seebeck siren (dotted) and pure tone siren (full line). The tests were carried out on different days with different temperatures, hence the shift in the positions of the maxima.

Helmholtz resonator (owing to a special orifice) had two free periods, of frequencies 82 and 93.† It will be seen at once that tones of these frequencies were constituents of the siren note when the speed was such that the frequencies of the fundamental were 41 and 47.

The ratios of the ordinates for these pairs of frequencies (after reducing

* We understand from Major Tucker that he hopes shortly to be allowed to publish a full account of his hot-wire microphone, which is at present confidential. Reference must be made to this paper for further details of the apparatus.

† Frequencies as low as these were employed because the tests were really only incidental experiments in a course of work, the application of which was entirely to low (aeroplane) notes.

their zero to the general level of the curve) are $45/74$ and $32/65$, or 0.61 and 0.49 , mean 0.55 . Before we compare this result with the calculated values of Table II, we must observe that the ratio thus measured is the ratio, not of the octave to the fundamental in a given note, but the ratio of a given tone, when it is the fundamental, to the same tone when it is the octave of the fundamental. If siren holes, q in number, are set along a circle of radius, r , and if the siren is making R revolutions per second, then $2\pi a/l = aq/r$, $x = 2\pi Rrt$, and the harmonic $S(2\pi na/l)\cos 2\pi nx/l$ becomes

$$S(naq/r) \cos 2\pi n Rqt.$$

In a test with a resonator, we compare the intensity of a certain tone when it is the fundamental ($n = 1$, $R = R_1$) with that of the same tone when it is the n th harmonic of the fundamental obtained by running the siren n times as slowly ($n = n$, $R = R_1/n$). The product nR has the same value in the two cases, and the ratio of the intensities is

$$\left(\frac{S(naq/r)}{S(aq/r)} \right)^2,$$

which differs from (11) in the absence of the n^2 factor. It is important not to overlook this point in analysing siren tests.

For the test in question, $q = 16$, $r = 6$. The diameter of the holes was $\frac{1}{2}$ inch but the air-supply tube was slightly smaller, $\frac{2}{5}$ inch. When the tube and holes have not the same diameter, the calculations of § 3 become much more elaborate, but it can be shown that if the diameters differ only slightly, a first approximation is obtained by taking for a the mean of the diameters. Thus in our case $a = 0.45$, and so $aq/r = 1.2$. The required ratio,

$$\left(\frac{S(2aq/r)}{S(aq/r)} \right)^2$$

is one quarter of the corresponding entry in Table II, and so is found to be $\frac{1}{4}(2.22)$ or 0.55 . This lies satisfactorily between the observed values. (In practice, the measured ordinates of the peaks are, unfortunately, not so sharply defined as the measured abscissæ.)

This agreement provides some verification of our theory, though much more exhaustive tests would be desirable. It is sufficient, however, to justify a use of the theory with some confidence in an attempt to design a siren to give a pure tone.

§ 5. *Construction of a Siren to give a Pure Tone.*—Accepting the general theory of a siren given above, to obtain a pure tone we should attempt to modify the shape of the holes, or of the cross-section of the supply tube, or both, so that the effective area of the orifice (the area common to tube and hole) is proportional to the sine of the displacement. It is clear at once that

this cannot be attained so long as the tube and holes have the same shape: for the maxima of the curve of effective area, which will occur when the tube exactly covers a hole, will always be sharp, as in fig. 1, the differential coefficient here changing suddenly from a non-zero positive value to a negative value.

If the orifice were reduced to a narrow straight slit,* and the boundary of the cut-out portion of the disc be itself a sine-curve (or double sine-curve), the object would be achieved. The use of a narrow slit for the orifice is, however, open to objections; there is difficulty in getting sufficient intensity unless the slit is made very long; further, there are mechanical difficulties in cutting a continuously sinusoidal hole, owing to the severing of the material, so that it can only be cut in the edge of the plate.

If, however, the orifice is altered merely to a *rectangular* section, the following construction (which is believed to be novel) may be adopted. Let a rectangular aperture of breadth a , and sufficient height to overlap all the ordinates concerned, pass over the region bounded between the curve $y = f(x)$ and the x -axis; and suppose that $f(x) = 0$ for $-a \leq x \leq 0$. Our requirement is then that

$$\int_{x-a}^x f(x) dx \propto 1 - \cos kx$$

for $x \geq 0$. Differentiating we have

$$f(x) - f(x-a) \propto \sin kx.$$

Omitting the constant of proportionality, we can now build up the following system of values of $f(x)$:—

$$f(x) = 0 \quad (-a \leq x \leq 0),$$

$$f(x) = \sin kx \quad (0 \leq x \leq a),$$

$$f(x) = \sin kx + \sin k(x-a) \quad (a \leq x \leq 2a),$$

$$f(x) = \sin kx + \dots + \sin k(x - \overline{p-1}a) \quad [(p-1)a \leq x \leq pa].$$

The period in x is $2\pi/k$; putting $2\pi k = na$, and summing the expression for $f(x)$, we find

$$f(x) = \frac{\sin p\pi/n}{\sin \pi/n} \sin \frac{2\pi}{n} \left(\frac{x}{a} - \frac{p-1}{2} \right) \quad (p-1 \leq x/a \leq p).$$

By the nature of the case, $f(x)$ must never be negative, and must be periodic in na ; it follows that n must be an integer, and that the last

* This has been suggested previously; see Koenig, 'Ann. der Phys. und Chem.,' 2nd series, vol. 14, p. 369 (1881). In this siren the edge of the disc had the form of a sine-curve; Koenig gives no evidence as to the real purity of the tones obtained.

equation must hold for values of p up to $n-1$; also, $f(x) = 0$ for $x/a = p = n-1$, and $f(x)$ must continue to be zero throughout the n th section. Examples of the complete graph of $f(x)$, for the two cases of n even and n odd, are shown in fig. 4 ($n = 6, n = 5$). The curious shape of the curve for n odd near its mid point is of some interest.

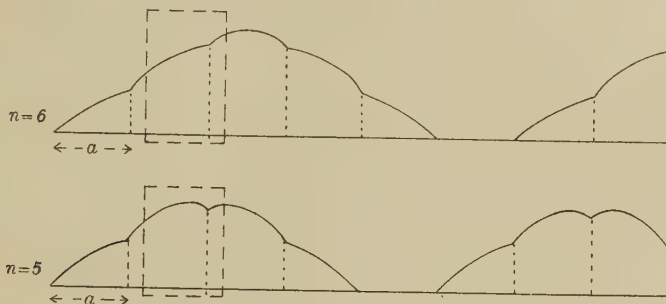


FIG. 4.—Calculated forms of holes for pure tone siren, with rectangular orifice (orifice shown dotted).

A siren disc of this type was constructed in Major Tucker's workshop; the disc was bored with twelve holes of the shape of the first diagram in

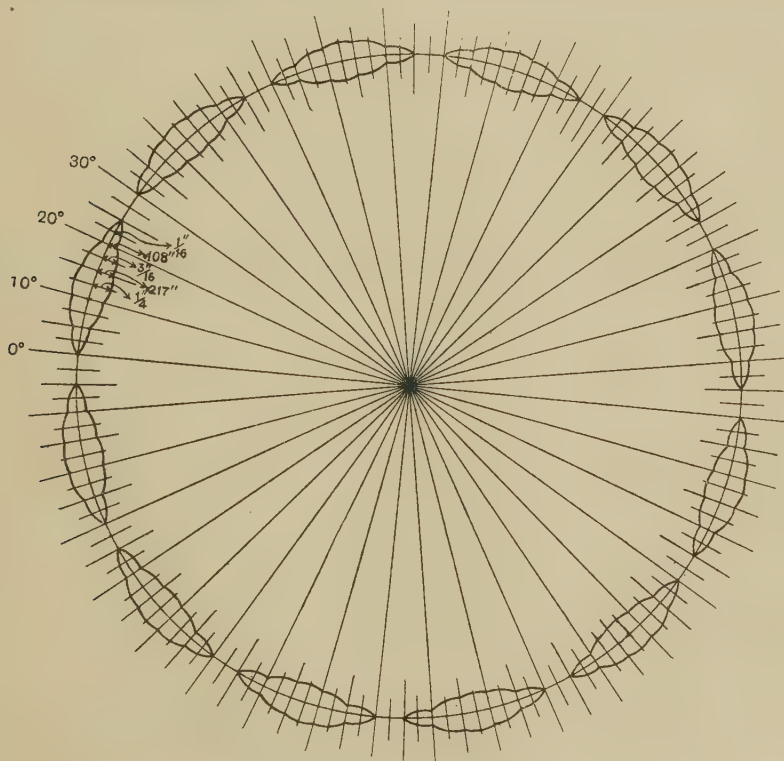


FIG. 5.—Disc of pure tone siren.

fig. 4, set round a circle of radius 4·3 inches, the ordinates being marked off radially* on each side of the base circle; a drawing of the complete disc is shown in fig. 5.

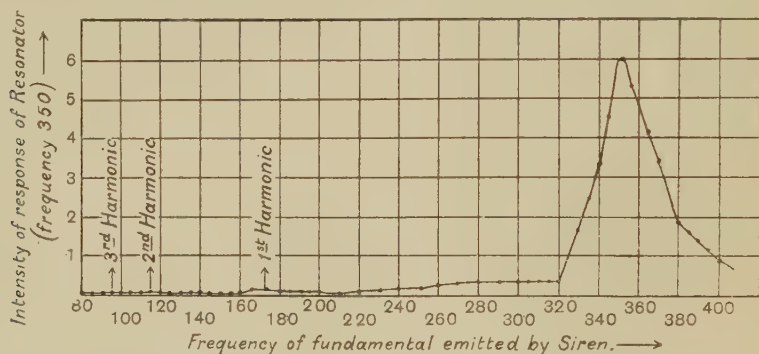


FIG. 6.—Test of purity of siren note (pure tone siren).

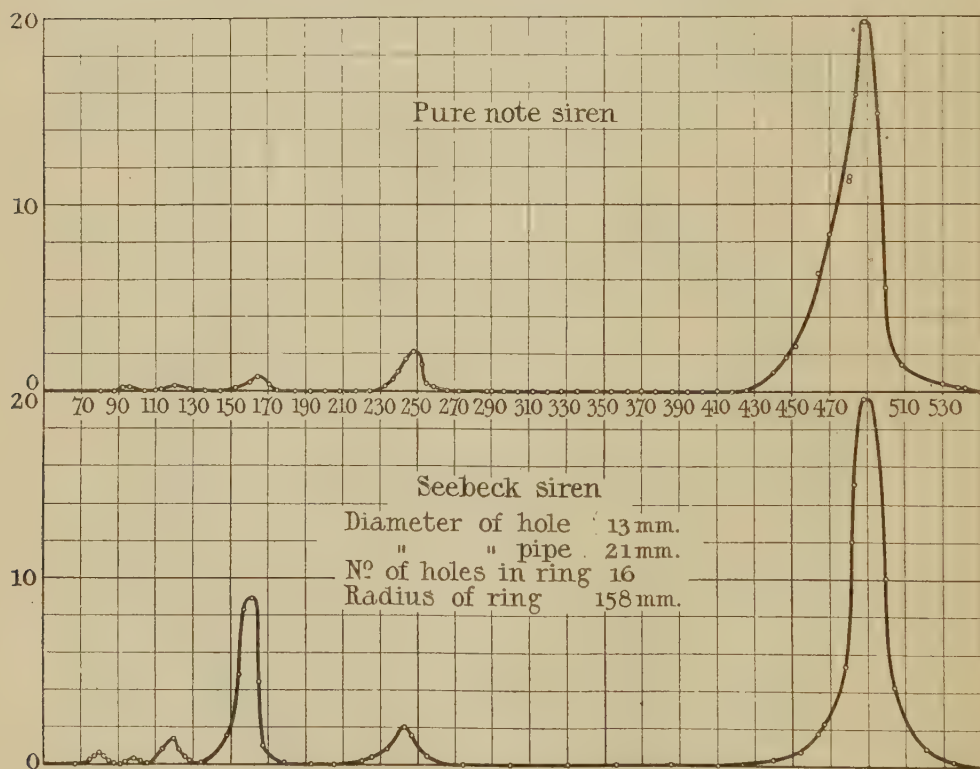


FIG. 7.—Comparative test of purity of notes, frequency 488.

* The analysis is easily modified to apply to the case of the circular base-line, but the actual corrections are small. The orifice is, of course, a section bounded by arcs and radii.

The results of tests of this siren with resonators are shown in figs. 3, 6, 7, for fundamentals of frequencies 80-90, 350, 488.

It will be seen that there is a marked improvement in the purity of the tone. The purity appears to be greater for the high frequencies than for the low ones; in fig. 3 the peak corresponding to the octave is about 7.5 per cent. of that corresponding to the fundamental (frequency 80 to 100); in fig. 4 (frequency 350) the fraction has diminished to 1 or 2 per cent. (It must be remembered, in accordance with § 4, that the ratios of the intensities of octave to fundamental in the actual notes must be four times these, namely, 30 per cent. and 4-8 per cent.) It would, perhaps, be expected that irregular disturbances and imperfections, leading to higher values for the later terms in the Fourier series, would be more prominent for low speeds than for high speeds. Even for the low speed, however, the first harmonic is about seven times as intense in the Seebeck siren used as in the new siren.

§ 6. *Summary.*—The ordinary siren can be regarded as a point source of air of variable flux, the flux being proportional to the area of the orifice exposed by the holes in the disc; in general, the tone from such a siren is far from pure. The relative intensities of the harmonics for a siren with circular holes and a circular orifice are calculated and compared with experiment; it is concluded that a fairly pure note should be obtained from a siren of this type in which the distance between the centres of adjacent holes is twice the diameter of the holes. If, however, the orifice is rectangular in section, the holes can be so shaped that the area of the orifice exposed varies exactly as the size of the displacement, such a siren should produce a very pure tone. Experimental tests of a siren constructed on these lines are quoted and discussed.

The Stability of Fluid Motion.

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1. The following notes on the stability of fluid motion arose from a desire to use the energy method, introduced by Reynolds and modified by Orr, as a measure of the comparative degree of stability of various types of flow under different boundary conditions. A few examples are worked out to illustrate this point of view: in § 5 a case which resembles the flow of a stream with a free surface; in § 7 flow which approximates to a uniform stream between fixed walls without slipping at the walls; in §§ 6, 8 motion with other boundary conditions. Before proceeding to these, it seems desirable to give a short account of the method in the form in which it is used later, together with some remarks on its relation to the classical method of small vibrations.

2. We shall consider only two-dimensional motion of an incompressible viscous fluid limited by the planes $y = \pm a$. Let the steady state under an assigned forcive and given boundary conditions be specified by a velocity, U , parallel to the axis of x . Let the disturbed state have velocity components $(U+u, v)$ and let the additional pressure be p . Then, by taking the difference of the two sets of hydrodynamical equations for the two states and neglecting squares and products of the additional velocities, we have

$$\begin{aligned}\frac{\partial u}{\partial t} + U \frac{\partial u}{\partial x} + v \frac{\partial U}{\partial y} &= -\frac{1}{\rho} \frac{\partial p}{\partial x} + \frac{\mu}{\rho} \nabla^2 u, \\ \frac{\partial v}{\partial t} + U \frac{\partial v}{\partial x} &= -\frac{1}{\rho} \frac{\partial p}{\partial y} + \frac{\mu}{\rho} \nabla^2 v,\end{aligned}\tag{1}$$

together with the equation of continuity.

It is convenient to introduce non-dimensional variables given by

$$x = a\xi; \quad y = a\eta; \quad a\tau = \bar{U}t;$$

where $\bar{U}$ is the mean velocity over the cross-section in the steady state. Further, we write UU instead of U , and take the current function of the additional velocity to be $\bar{U}a\psi$. Eliminating p from the two equations (1), we obtain

$$R \left(\frac{\partial}{\partial \tau} + \frac{\partial}{\partial \xi} \right) \nabla^2 \psi - RU'' \frac{\partial \psi}{\partial \xi} = 2 \nabla^4 \psi,\tag{2}$$

where U'' is written for $d^2U/d\eta^2$, and R is Reynolds' number $2a\bar{U}/\nu$. There are in addition the appropriate boundary conditions for the disturbing function, ψ . The classical method of examining the stability of a given

distribution U consists in assuming a solution of (2) of the form $\exp. \{i(n\tau + p\xi)\} f_n(\eta)$. For any arbitrary real value of p , the corresponding possible forms of $f_n(\eta)$ and values of n are found from (2) together with the boundary conditions. The distribution U may be said to be thoroughly stable if every possible value of n has a positive imaginary part, and if this holds for all positive values of R .

The usual boundary conditions, which we shall assume in the first place, are $u = 0, v = 0$, or

$$\psi = 0; \quad \partial\psi/\partial\eta = 0: \quad \eta = \pm 1. \quad (3)$$

From the work of Kelvin, Rayleigh, Orr, Hopf, and others, it may be taken that the simple shearing motion, $U = 1 + \eta$, is thoroughly stable in this sense; and probably a similar conclusion holds for motion under a constant force or pressure gradient, namely $U = \frac{3}{2}(1 - \eta^2)$.

There are various possible explanations of the well-known divergence between these results and the behaviour of actual fluids. In the first place, it is obvious that the physical properties, whether of the fluid or of the walls, are inadequately specified in the mathematical statement of the problem. But, apart from this, the disturbances have been supposed small, and second order terms neglected. Again, in a system of this type, a disturbance may be small initially and may converge ultimately to zero, but may be very large at intermediate times, and may thus give rise to practical instability.

The energy method of Reynolds is in a different category from these in that it takes the mathematical problem as it stands and does not necessarily involve the actual magnitude of the disturbance; in fact, it forms a new criterion or measure of degree of stability. The energy of the disturbance being defined by

$$E = \frac{1}{2} \rho a^2 \bar{U}^2 \iint \left\{ \left(\frac{\partial\psi}{\partial\xi} \right)^2 + \left(\frac{\partial\psi}{\partial\eta} \right)^2 \right\} d\xi d\eta, \quad (4)$$

we have from (2) and (3), after integrating by parts,

$$\frac{dE}{dt} = \frac{1}{2} \mu \bar{U}^2 \left[R \iint U' \frac{\partial\psi}{\partial\xi} \frac{\partial\psi}{\partial\eta} d\xi d\eta - 2 \iint (\nabla^2\psi)^2 d\xi d\eta \right]. \quad (5)$$

Here dE/dt means the rate of increase of E in a region whose end boundaries move with the steady velocity U . We may replace this by $\partial E/\partial t$ for a region with fixed ends, and we shall then have additional terms on the right of (5) denoting flux of energy across these ends. The latter terms may be omitted under conditions which cover the usual cases: namely, either the disturbance is periodic in ξ , or it is limited or localised so that ψ and its derivatives converge sufficiently rapidly to zero for $\xi = \pm\infty$. We shall assume such conditions to hold in what follows, and references to boundary conditions mean those which hold at the planes $\eta = \pm 1$.

Reynolds' method of using (5) to determine a criterion of stability consisted in assuming a suitable form for ψ and finding the least value of R for which the right-hand side of (5) is zero. It is usually stated that this method assumes turbulent motion to be already in existence, and it then gives a criterion to show whether the turbulence is increasing or decreasing momentarily; but this is somewhat misleading without defining what is meant by turbulent motion. Equation (5), as stated above, applies to any small arbitrary disturbance, neglecting terms of the second order, as in the ordinary method of small vibrations; further, U is a laminar fluid motion satisfying the usual hydrodynamical equations under the given conditions.

On the other hand, Reynolds defined U as the mean velocity at each point, taken over a small region or during a short time, and this principal or mean motion need not satisfy the ordinary equations. The extra velocities u and v then play a double part, in that they specify the disturbance, and at the same time give a measure of the turbulence; they must satisfy certain conditions as to their mean values, and then equation (5) holds in the same form when mean values are used. However, in applying it to find the criterion for flow under a constant pressure gradient, Reynolds, and Sharpe following him, did, in fact, take U to be the usual form, $C(\alpha^2 - y^2)$, for steady laminar flow. But in turbulent flow, although the variations of velocity at any point are small, yet they may cause the gradient of the mean velocity to differ appreciably from its value in laminar flow, as is obvious from a comparison of the curves of distribution of velocity across a pipe in regular and in turbulent flow.

However, it is unnecessary to dwell on this distinction, as it has been pointed out clearly by Lorentz* and other writers; further, we shall consider here only small disturbances.

3. Under these circumstances, the energy method has been given a precise and definite meaning by Orr† from the following considerations:—

If the right-hand side of (5) is positive, the energy of the disturbance is momentarily increasing. But, for a given velocity distribution, U , it may be impossible to find any function, ψ , satisfying the boundary conditions, such that that expression is positive, unless R exceeds a certain value. If such be the case, this least value of R is a critical value of definite significance. The corresponding critical disturbance is found by taking the variation of the equation

$$R \iint U' \frac{\partial \psi}{\partial \xi} \frac{\partial \psi}{\partial \eta} d\xi d\eta - 2 \iint (\nabla^2 \psi)^2 d\xi d\eta = 0, \quad (6)$$

subject to $\delta R = 0$.

* H. A. Lorentz, 'Abhandlungen über Theor. Phys.,' vol. 1, p. 43.

† W. McF. Orr, 'Proc. Roy. Irish Acad.,' vol. 27, p. 9 (1907).

Carrying out the variation, and using the boundary conditions (3), we obtain

$$4\nabla^4\psi + 2RU' \frac{\partial^2\psi}{\partial\xi\partial\eta} + RU'' \frac{\partial\psi}{\partial\xi} = 0. \quad (7)$$

To find the critical value of R , we assume first that ξ occurs in ψ as a factor $\exp. ip\xi$, and then solve (7); using the boundary conditions, we have an equation from which we can find the least value of R for a given value of p , and finally we take the minimum value of R with respect to p .

The process has been expressed in a different form by Hamel.* Using the corresponding Green's function for the equation $\nabla^4\psi = 0$, the equation (7) may be replaced by a linear integral equation for ψ , of which the required value of R is the lowest characteristic number.

Returning to equation (5), if dE/dt is positive for any assigned initial disturbance, it does not follow that the motion is unstable in the ordinary sense. But, if there exists an absolute minimum for R in the manner explained above, it follows that, when R is less than this value, dE/dt is negative for every initial disturbance, and must always remain negative. Thus the system has at least a much higher degree of stability for such values of R compared with those greater than the critical minimum. Obviously, this method does not produce any new information which is not implicit in the ordinary equations, such as equations (2) and (3); but it presents part of that information in a different form, so that the critical minimum of R may be used as a measure of the degree of stability of various distributions of velocity under different boundary conditions.

4. It is convenient to classify the boundary conditions under which the energy equation (5) is valid. For this purpose we use an alternative form derived directly from equations (1), with the ordinary notation

$$p_{xx} = -p + 2\mu \frac{\partial u}{\partial x}; \quad p_{xy} = \mu \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right); \quad p_{yy} = -p + 2\mu \frac{\partial v}{\partial y}, \quad (8)$$

We have

$$\begin{aligned} \frac{dE}{dt} = & \int \{u(lp_{xx} + mp_{xy}) + v(lp_{xy} + mp_{yy})\} ds - \rho \iint uv \frac{dU}{dy} dx dy \\ & + \iint \left\{ p_{xx} \frac{\partial u}{\partial x} + p_{yy} \frac{\partial v}{\partial y} + p_{xy} \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right) \right\} dx dy, \end{aligned} \quad (9)$$

where ds is a line element of the boundary and (l, m) the normal.

We have specified the conditions at the end boundaries, and we are concerned now with the planes $y = \pm a$. It follows that we get the energy

* G. Hamel, 'Gött. Nachr., Math. Phys. Klasse,' 1911, p. 261.

equation (5), without any surface integrals expressing transfer of energy across the boundaries, with the following combinations:

(i) $u = 0, v = 0$; (ii) $u = 0, p_{yy} = 0$; (iii) $v = 0, p_{xy} = 0$; (iv) $p_{xy} = 0, p_{yy} = 0$.

We may also verify that, under these conditions, the variation of (6) leads to the same differential equation (7).

5. Most of the fluid motions whose stability has been examined, come under case (i) of the above. A different case of special interest is a stream with a free upper surface, the conditions at the upper surface being as in (iv). These conditions, however, do not lead to simple expressions in terms of the disturbing function, ψ ; moreover it is not permissible to regard the upper free surface as rigorously plane. We therefore, following Kelvin,* replace the problem by one which is very nearly the same but is more easily specified; it may be described as a broad river flowing over a perfectly smooth inclined plane bed, the upper surface being fitted by a parallel plane cover moving with the water in contact with it. The conditions at the upper surface then come under case (iii) of the previous section.

We take the origin in the upper surface in this case, so that a is the depth of the stream and R is $a\bar{U}/\nu$. The steady state is given by

$$U = \frac{3}{2}(1 - \eta^2). \quad (10)$$

Using this in (7) and assuming ψ to be proportional to $e^{ip\xi}$, the differential equation becomes

$$\left(\frac{d^2}{d\alpha^2} - 1\right)^2 \psi - k \left(2\alpha \frac{d\psi}{d\alpha} + \psi\right) = 0, \quad (11)$$

where $\alpha = p\eta$, and $k = 3iR/2p^3$.

The boundary conditions are $u = 0, v = 0$ at the bed of the stream, and $v = 0, p_{xy} = 0$ at the upper surface; these reduce to

$$\begin{aligned} \psi &= 0, \quad d^2\psi/d\alpha^2 = 0; & \alpha &= 0; \\ \psi &= 0, \quad d\psi/d\alpha = 0; & \alpha &= p. \end{aligned} \quad (12)$$

Equation (11) was solved by Orr for flow between two fixed planes with u and v zero at both boundaries, and it was found necessary to consider only solutions in even powers of α . We shall require here the corresponding solutions in odd powers. Writing a solution in the form

$$\psi = \sum A_n \alpha^n / n!$$

we have the sequence relation

$$A_{n+4} - 2A_{n+2} + \{1 - (2n+1)k\}A_n = 0. \quad (13)$$

* Kelvin, 'Math. and Phys. Papers,' vol. 4, p. 330.

Denoting by $\psi_0, \psi_1, \psi_2, \psi_3$ the solutions beginning with $1, \alpha, \alpha^2, \alpha^3$ respectively, it follows from (12) that the boundary conditions lead to

$$\psi_1 d\psi_3/d\alpha - \psi_3 d\psi_1/d\alpha = 0 \quad (14)$$

where α has to be replaced by p .

Calculating the coefficients far enough to give sufficient accuracy for our purpose, we have

$$\begin{aligned} \psi_1 &= \alpha + 2\alpha^3/3! + (3+3k)\alpha^5/5! + (4+20k)\alpha^7/7! \\ &\quad + (5+70k+33k^2)\alpha^9/9! + (6+180k+366k^2)\alpha^{11}/11! \\ &\quad + (7+385k+2029k^2+627k^3)\alpha^{13}/13! + (8+728k+7832k^2+9672k^3)\alpha^{15}/15! \\ &\quad + (9+1260k+24030k^2+73500k^3+16929k^4)\alpha^{17}/17! + \dots, \\ \psi_3 &= \alpha^3/3! + 2\alpha^5/5! + (3+7k)\alpha^7/7! + (4+36k)\alpha^9/9! \\ &\quad + (5+110k+105k^2)\alpha^{11}/11! + (6+260k+894k^2)\alpha^{13}/13! \\ &\quad + (7+525k+4213k^2+2415k^3)\alpha^{15}/15! + (8+952k+14552k^2 \\ &\quad \quad \quad + 28968k^3)\alpha^{17}/17! + \dots \end{aligned}$$

Forming equation (14) we have

$$\begin{aligned} &2/3! + 8p^2/5! + 32p^4/7! + 128p^6/9! + (512+192k^2)p^8/11! \\ &\quad + (2048+2244k^2)p^{10}/13! + (8192+19456k^2)p^{12}/15! \\ &\quad + (32768+139264k^2)p^{14}/17! + (131072+901120k^2 \\ &\quad \quad \quad + 129024k^4)p^{16}/19! + \dots = 0. \quad (15) \end{aligned}$$

Only even powers of k appear in this equation, thus giving a check upon the arithmetic; further, the terms independent of k may be summed. Taking the least root of (15) as an equation for k^2 , we have approximately

$$R^2 = \frac{\sinh 2p - 2p}{9p^5 \left(\frac{192}{11!} + \frac{2244p^2}{13!} + \frac{19456p^4}{15!} + \frac{139264p^6}{17!} + \frac{901120p^8}{19!} + \dots \right)}. \quad (16)$$

Instead of forming an equation for the minimum value of R , it is simpler to find it by trial. We find, with sufficient accuracy, that it occurs near $p^2 = 11$, and then, approximately,

$$R = 96. \quad (17)$$

The corresponding value, found by Orr, for flow under similar conditions but with a fixed plane at the upper surface, is 117. We conclude then that flow in an open canal has a lower degree of stability than flow between fixed planes.

Turning to experimental results, the number usually quoted for flow through a tube is 2000 approximately. This was obtained chiefly from

experiments with smooth glass tubes; a much lower number, of the order of 400, has been found from metal tubes. The only available direct results for flow in an open stream appear to be those given by Hopf,* who found R to be of the order of 300. These results agree in character with the theoretical calculations, which is all that could be expected.

It is of interest to note that this appears to contradict a statement by Reynolds† in one of his earlier papers. He classes separately circumstances conducive to steady motion and those conducive to unsteady motion: among the former a free surface, and in the latter solid bounding walls. However, this opinion seems to be based on visual observation of eddies caused by the wind beneath the oiled surface of water. "At a sufficient distance from the windward edge of an oil-calmed surface there are always eddies beneath the surface, even when the wind is light. . . . Without oil I was unable to perceive any indication of eddies."

This introduces a different property of a boundary surface, namely, that of initiating disturbances. The mathematical statement ignores this property and specifies only control of the velocity functions: the disturbances are supposed to be initiated by some extraneous agency, and it is tacitly assumed that all types of disturbance are equally probable. It may be, for instance, that the theoretical results for flow through pipes should be compared with experiments on rough pipes rather than those with perfectly smooth walls. However, we may conclude that a solid boundary is conducive to stability in so far as it ensures that there is no slipping of the fluid in contact with it.

6. In determining the minimum value of R from the differential equation (7), there are only two factors: the distribution of steady velocity, U , and the boundary conditions for the disturbance. The comparison in the previous section, between an open stream and flow between fixed walls, involved changes in both these factors. We may separate the effect of the boundary conditions by assuming the same value of U as in (10), but expressing the property of the supposed moving plane in contact with the upper surface by $u = 0, v = 0$, instead of by $v = 0, p_{xy} = 0$. To anticipate the argument of the next sections, we should expect a value of R intermediate between 96 and 117.

We have the same equation (11) for ψ , together with $\psi = 0, d\psi/d\alpha = 0$ at $\alpha = 0$, and $\alpha = p$. It follows that only the solutions ψ_2 and ψ_3 are involved, and we have

$$\psi_2 d\psi_3/d\alpha - \psi_3 d\psi_2/d\alpha = 0, \quad (18)$$

* L. Hopf, 'Ann. der Phys.,' vol. 32, p. 777 (1910).

† O. Reynolds, 'Scientific Papers,' vol. 2, pp. 157, 59. See also A. H. Gibson, 'Phil. Mag.,' vol. 25, p. 81 (1913).

when $\alpha = p$. The series for ψ_3 is given in §5; also we have

$$\begin{aligned}\psi_2 = & \alpha^2/2! + 2\alpha^4/4! + (3+5k)\alpha^6/6! + (4+28k)\alpha^8/8! \\ & + (5+90k+65k^2)\alpha^{10}/10! + (6+220k+606k^2)\alpha^{12}/12! \\ & + (7+455k+3037k^2+1365k^3)\alpha^{14}/14! + (8+840k+10968k^2 \\ & + 17880k^3)\alpha^{16}/16! + \dots\end{aligned}$$

The boundary equation (18) leads to

$$\begin{aligned}2/4! + 8p^2/6! + 32p^4/8! + 128p^6/10! + (512+280k^2)p^8/12! \\ + (2048+3136k^2)p^{10}/14! + (8192+25216k^2)p^{12}/16! \\ + (32768+174080k^2)p^{14}/18! + \dots = 0. \quad (19)\end{aligned}$$

The minimum value of R seems to occur for about $p^2 = 12$, though it is not a sharply defined minimum; however, with a similar approximation as in previous cases, we find the critical minimum of R to be 110.

7. It is well known that, when fluid motion through a tube has changed from laminar to turbulent flow, the distribution of mean velocity over the cross-section alters so that the velocity becomes more nearly uniform over the greater part of the section, while falling to zero at the walls. This suggests a study of the comparative stability when the distribution of velocity alters in this manner, the boundary conditions being unchanged.

However, it must be noted that we assume the distribution to be a steady state which has been acquired under a law of force, which may be determined from the hydrodynamical equations, so as to give the required form for U .

A simple form, which illustrates the points in question, is

$$U = (1 + 1/2n)(1 - \eta^{2n}). \quad (20)$$

As n is made larger, the velocity approximates more closely to the mean velocity, $\bar{U}$, over the greater part of the cross-section, while remaining zero at the walls. The corresponding law of force is, in the usual notation,

$$X = \nu(4n^2 - 1)(U/a^2)\eta^{2n-2}. \quad (21)$$

The greater the value of n , the more is the field of force concentrated near the walls, quite apart from the value of the viscosity. The flow approximates to a uniform stream, but retaining the condition of zero velocity at the walls.

The usual case of flow under a uniform field of force is given by $n = 1$. It is sufficient for comparison to work out another numerical case, say $n = 2$. We have then

$$U = \frac{5}{4}(1 - \eta^4). \quad (22)$$

Equation (7) becomes

$$\left(\frac{d^2}{d\alpha^2} - 1\right)^2 \psi - 2k \left(2\alpha^3 \frac{d\psi}{d\alpha} + 3\alpha^2 \psi\right) = 0, \quad (23)$$

where $k = 5iR/8p^5$.

The boundary conditions are

$$\psi = 0; \quad d\psi/d\alpha = 0; \quad \alpha = \pm p.$$

Solving (23) by a power series $\Sigma A_n \alpha^n/n!$, we have

$$A_{n+6} = 2A_{n+4} - A_{n+2} + 2k(n+1)(n+2)(2n+3)A_n. \quad (24)$$

As in the simpler cases, it is sufficient to choose fundamental solutions involving only even powers of α ; denoting these by ψ_0 and ψ_2 we have

$$\begin{aligned} \psi_0 &= 1 + \alpha^2/2! + \alpha^4/4! + (1+12k)\alpha^6/6! + (1+192k)\alpha^8/8! \\ &\quad + (1+1032k)\alpha^{10}/10! + (1+3552k+20160k^2)\alpha^{12}/12! + (1+9492k \\ &\quad + 696960k^2)\alpha^{14}/14! + (1+21504k+8162256k^2)\alpha^{16}/16! + \dots \\ \psi_2 &= \alpha^2/2! + 2\alpha^4/4! + 3\alpha^6/6! + (4+168k)\alpha^8/8! + (5+1656k)\alpha^{10}/10! \\ &\quad + (6+8184k)\alpha^{12}/12! + (7+28392k+574560k^2)\alpha^{14}/14! \\ &\quad + (8+78960k+11204352k^2)\alpha^{16}/16! + (9+188496k \\ &\quad + 102266496k^2)\alpha^{18}/18! + \dots \end{aligned}$$

From the boundary condition

$$\psi_0 d\psi_2/d\alpha - \psi_2 d\psi_0/d\alpha = 0,$$

we obtain the equation

$$\begin{aligned} p + 2p^3/3! + 8p^5/5! + 32p^7/7! + 128p^9/9! + 512p^{11}/11! \\ + (2048 + 129024k^2)p^{13}/13! + (8192 + 3280896k^2)p^{15}/15! \\ + (32768 + 7753296k^2)p^{17}/17! + \dots = 0. \quad (25) \end{aligned}$$

Using this as an equation for R , we find by trial that the minimum value occurs near $p^2 = 3$; and the critical minimum value of R is 280 approximately.

The corresponding value for the ordinary parabolic distribution ($n = 1$) is 117. Thus, the critical value of R increases as the flow approximates more closely to a uniform stream, without slipping at the walls; and, in this sense, the motion becomes increasingly stable.

8. It has been stated that, under the boundary conditions $u = 0, v = 0$, there is thorough stability, in the ordinary sense, for simple shearing motion and probably also for laminar flow between fixed planes. In view of the behaviour of actual fluids in similar conditions, another suggestion has been put forward by Hopf.* He proposes to express the influence of a wall by making the extra normal pressure, due to the disturbance, constant at the

* L. Hopf, 'Ann. der Phys.,' vol. 59, p. 538 (1919).

wall, together with no tangential slipping; in fact, his boundary conditions come under case (ii) of § 4, namely $u = 0$, $p_{yy} = 0$. With these assumptions, he applies the method of small vibrations to simple shearing motion between a fixed plane and a parallel moving plane. It appears that the motion is unstable for disturbances whose wave-length exceeds a certain value; for smaller wave-lengths it is stable or unstable according to the value of R . Thus the motion is not thoroughly stable. Without discussing how far these assumptions express the behaviour of actual fluids and boundaries, we may see how they affect the energy method.

We shall take the case of laminar flow between fixed planes, for which the previous calculations are available.

The stream function ψ satisfies equation (11), and the boundary conditions are

$$u = 0; \quad -p + 2\mu \partial v / \partial y = 0.$$

From the equations (1), these are equivalent to

$$u = 0; \quad \rho v dU/dy - \mu \partial^2 u / \partial y^2 = 0,$$

or, in the present notation,

$$d\psi/d\alpha = 0; \quad d^3\psi/d\alpha^3 - 2k\alpha\psi = 0; \quad \alpha = \pm p. \quad (26)$$

Using the solutions ψ_0 and ψ_2 , these give

$$\psi_0'(\psi_2''' - 2kp\psi_2) - \psi_2'(\psi_0''' - 2kp\psi_0) = 0, \quad (27)$$

where accents denote differentiation with respect to α .

From the previous work, this equation involves odd powers of k . But k is $3iR/4p^3$ and we have to determine R in terms of p from (27). It follows that in this case there is no real solution of the problem of finding the critical minimum of R .

It seems probable that it is only those motions which are completely stable in the ordinary theory which lead also to a real minimum for R . The suggestion may be stated in this manner: if a fluid motion is thoroughly stable when considered by the method of small vibrations applied to equation (2) and the boundary conditions, then it also possesses a real minimum value of R found from equation (7) and the boundary conditions. It has been pointed out that the latter equation is derived directly from the former, and it may be presumed that the minimum value of R depends in some manner upon the rates of decay of elementary vibrations and so may be used as a measure of the degree of stability of the system.

OBITUARY NOTICES
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Raschke

JOHN WILLIAM STRUTT, BARON RAYLEIGH, 1842—1919.

THE position to be assigned to a man of science in the history of his subject cannot be estimated solely by his published work. The record of that work is permanent; its merit may be judged as well a hundred years hence as it is at present. But there is an invisible element in the fruition of creative power which only the testimony of contemporaries can save from oblivion, because it depends on character as well as on genius and ability. Men have risen to posthumous fame, deserved but dimmed by some shadow of failure because their lives left no impression on the intellectual level of their time. Such men possessed to an exceptional degree that immunity from the influence of current thought which is the essence of originality, but they were the slaves rather than the masters of their own individuality. To receive inspiration as well as to impart it, to stimulate thought at the right moment, to keep in touch with others without losing independence requires human sympathy as well as originality, and it was the combination of the two qualities, each strong in itself and further strengthened by being linked to the other, that has been the outstanding feature of Lord Rayleigh's work. The life of such a man cannot be treated as an independent unit, for it is too intimately connected with the general progress even of those branches of knowledge with which it did not directly concern itself.

It is essential, therefore, to give a brief account of the position of Physics at the time Lord Rayleigh began work. When he took his degree in 1865, the conception of a strictly mechanical construction of the Universe had received strong support through the successes of the undulatory theory of light and the foundation of thermodynamics. Though foreshadowed to some extent in the laws of motion of Galileo and Newton, the principle of the Conservation of Energy had only recently found general acceptance. Men still in the prime of life remembered the days when Joule's experiments were looked upon with distrust, and his views on the nature of heat as heterodox. William Thomson, the future Lord Kelvin, barely forty years old, was in the zenith of his activity, and it was mainly through his efforts that the second law of thermodynamics was formulated while Rayleigh was at school. About the time he entered the University, Maxwell applied the laws of probability to the kinetic theory of gases, and while he was getting ready for his Tripos, the same author's great paper on "A Dynamical Theory of the Electromagnetic Field" was communicated to the Royal Society. The undulatory theory of light had been placed on a sound dynamical basis by Green and Stokes. Though Foucault had disposed of all remaining doubts by showing experimentally that light was propagated through water more slowly than through air, there were some few sceptics still.—Faraday was alive, though deprived of his intellectual powers and nearing his death.

On the purely experimental side, though much valuable work was being done in testing and confirming theories, the discovery of Spectrum Analysis was the only fresh departure in Physics. As such it created as great an interest and was as fruitful in disclosing new facts as the more fundamental discoveries of our own time. The spectra of stars had only just begun to be examined, and the nature of the solar prominences seen during total eclipses was on the point of being revealed. The peculiar luminous appearances observed when electric discharges were made to pass through vacuum tubes had only been incompletely observed, and no attempt had been made to bring them into relationship with other physical phenomena. Photography, as it is now understood, was in its infancy, and many experimental appliances now accepted as almost household utensils were either unknown or of recent origin. The Bunsen burner was only eight years old.

Such was the foundation on which Rayleigh began to build.

The Rayleigh Peerage dates from 1821, when it was bestowed on the wife of Colonel Joseph Holden Strutt as Baroness Rayleigh, in recognition of her husband's eminent services in raising and organising militia regiments. Colonel Strutt sat as M.P. for Maldon from 1790 to 1826, and for Okehampton from 1826 to 1830. It was at his special request that the peerage offered to him was conferred on his wife (a daughter of the Duke of Leinster). When the first Lady Rayleigh died, in 1826, the peerage descended to her son, John James, during the lifetime of his father. He married, in 1842, Clara Elizabeth La Touche, daughter of Captain Vicars, R.E., and on the 12th of November in the same year their first son was born.

The early education of John William Strutt was frequently interrupted by ill health. He entered Eton at the age of ten, but stayed there only for part of a year. Later he went for a short time to Harrow. Ultimately he was sent to Torquay, to be prepared for the University by Mr. Warner, who was the first to recognise his great intellectual powers, and allowed him special privileges in doing his lessons.

The future Lord Rayleigh, having entered Trinity College, Cambridge, as fellow-commoner on Dr. Lightfoot's side, in October, 1861, began his University career apparently without expectations of a high place, but his confidence gradually increased as he proceeded in his studies. His colleagues recognised his ability, and among the pupils of Routh he was looked upon as the most likely to come out as Senior Wrangler. In the annual college examinations he always occupied a high place, though his marks fell considerably short of those who stood at the top of the list. It is to be observed, however, that the examinations included classical and other subjects, and it was understood that in 1864 Strutt was easily first in mathematical papers. Among his recreations were tennis and photography. Though the old wet plate process afforded some opportunities for the practice of manual skill, Rayleigh severely felt the absence of any provision in the University curriculum for experimental work. After taking his degree, he went through a course of chemical analysis under Liveing, but otherwise found no

opportunity to become acquainted with the realities of scientific facts by personal observation.

In October, 1864, Rayleigh obtained the Sheepshanks Astronomical Exhibition, which was open to the competition of all undergraduates. In January, 1865, he took his degree as Senior Wrangler.

The examiners in the Tripos were: William Watson and Michael Marlow Umfreville Wilkinson; the Moderators: Isaac Todhunter and George Richardson. Geometrical Optics took a prominent place in the questions devoted to Mathematical Physics, and there was one question in Physical Optics which deserves mention, because it shows that the possibility of detecting the earth's motion through space by optical means had already been raised, and negatived so far as first order effects are concerned:

"Fresnel supposes that, when bodies move in the medium, the relative velocity of the medium with respect to the body is in the same direction, but in proportion $1:\mu$. Show that the retardation of a plate of glass will be independent of the motion of the earth, if the square of the velocity of the earth to the velocity of light be neglected."

The papers for the Smith's Prize do not reveal any very distinctive features, though more attention is given to contemporary investigations in the questions set by Whewell. One of them deals with the correction of the error of compasses due to the magnetisation of ships, and there is a sting in the tail of another, evidently referring to Lord Kelvin's arguments relating to the history of the earth: "If the heat (*sic*) of the earth's material increases as we descend, what reasoning may be founded upon this as to the history of the earth? How far are these reasonings sound?"

Rayleigh's scientific activity may for convenience be divided into five periods. The division is naturally not a sharp one; work prepared in one of the periods was often published in the next, and, especially during the later years, old problems were again taken up and carried a step forward. The first period extends up to the time when he took up the Cavendish Professorship, and may be taken to include most of the researches contained in the first volume of his 'Scientific Papers.' The second period is dominated by his work on electrical standards. The third period, which bridges over the interval between his departure from Cambridge and the experiments which led to the discovery of Argon, covers to a great extent his tenure of the Secretaryship of the Royal Society. The fourth, or "Argon," period was followed by one of great fertility, but no further distinction can be drawn, and it must be taken to extend to the time of death.

Four years elapsed between the degree examinations and the publication of Rayleigh's first paper. This, and others that followed at short intervals, show an extensive knowledge, not only of the current literature of the problems discussed, but of their historical development. We may already trace in them the chief features of the method of treatment to which he adhered throughout his life. While the subject is looked upon from the most general point of view, the results are illustrated by special applications that

may be, and most frequently are, verified experimentally. The problem is always concisely stated, and the mathematical discussion is reduced to its simplest form by the omission of all that is not important. If we were called upon to define the quality of Rayleigh's work, which forms its characteristic feature and marks his individuality, we should, I think, agree that it lay in his unflinching sense of what is essential in each problem, while he courageously left accessory complications to take care of themselves. Rayleigh himself recognised that his special gifts lay in that direction.

The first paragraph of his paper on "Some Electromagnetic Phenomena considered in connection with the Dynamical Theory" deserves quotation in full, because it is probably the only example in the history of science in which the first few lines, written by a young man for publication, are so typical of the procedure to which he adhered throughout his life :—

"It is now some time since the general equations applicable to the conditions of most electrical problems have been given, and attempts, more or less complete, have been made to establish an analogy between electrical phenomena and those of ordinary mechanics. In particular, Maxwell has given a general dynamical theory of the electromagnetic field, according to which he shows the mutual interdependence of the various branches of the science, and lays down equations sufficient for the theoretical solution of any electrical problem. He has also, in scattered papers, illustrated the solution of special problems by reference to those which correspond with them (at least, in their mathematical conditions) in ordinary mechanics. There can be no doubt, I think, of the value of such illustrations, both as helping the mind to a more vivid conception of what takes place, and to a rough quantitative result, which is often of more value, from a physical point of view, than the most elaborate mathematical analysis. It is because the dynamical theory seems to be far less generally understood than its importance requires, that I have thought that some more examples of electrical problems, with their mechanical analogues, might not be superfluous" ('Scientific Papers,' vol. 1, p. 1).

The paper that follows these introductory lines bears the imprint of the craftsman, marked as clearly as a picture by Perugino carries the signature of the artist in every square inch.

The first illustration of the principle enunciated in the opening paragraphs is derived from an experiment made by De La Rive "in which a battery (such as a single Daniell cell), whose electromotive force is insufficient to decompose water, becomes competent to do so by the intervention of a coil or electromagnet." It is shown that the behaviour of the electrical appliance is closely analogous to Montgolfier's hydraulic ram, and it is pointed out that if the pipe of the ram which provides for the escape of the water were closed, it would be unable to withstand the shock, and, after yielding within the limits of its elasticity, it would burst.

This bursting is compared with the passage of a spark at the place where a circuit carrying an electric current is broken. It will be seen that the explanation of this and other illustrations that are given depends on a true appreciation of electromagnetic momentum, and it must be remembered that at the time it was written there was still a widespread impression that absence of inertia was the characteristic property distinguishing electricity from ordinary matter. The simple manner in which Lord Rayleigh determines the mechanical value of the spark of an interrupted electric current by making use of electromagnetic momentum and energy still deserves to be studied by every student of science.

In a later part of the same paper, attention is drawn to a mechanical theorem of Thomson (Lord Kelvin), which leads directly to the solution of many electrical problems connected with induction. When applied to electrodynamics, the theorem states that whenever a current is suddenly generated in one of the systems, the initial current in all the others is determined by the condition that the energy of the field is a minimum. Interesting illustrations of the applications of this theorem are given.

The latter part of the paper contains the experimental verification of what at first sight looked like a paradox. If a secondary coil be wound round a primary, theory indicated that the initial current in the secondary, induced by the break of the primary current, should be greater the smaller the number of windings in the secondary; the reason being that its self-induction increases as the square of the number of windings, while the mutual induction increases only as the first power. The conclusion cannot be tested by a galvanometer because its indications depend not merely on the measure of the initial current, but also on the rate at which it subsequently falls off. It appeared probable, on the other hand, that the greater initial current might be made apparent through its magnetising effects. After a number of trials, the failure of which was traced to the insufficient suddenness of the break, a condenser was applied at the break like that of an induction coil, and the theoretical result could then be verified.

Most investigators would have been satisfied with this confirmation, but with characteristic caution Rayleigh returned to the subject in a second paper. He looked with suspicion on the introduction of a condenser, because its action was not completely understood. Unknown effects might complicate and vitiate the result. The previous conclusions were therefore confirmed by another experimental arrangement. The concluding paragraphs of the second paper are devoted to a discussion of the action of the condenser in the inductorium, and the opinion is expressed that it is "by no means a complete account of the matter to say that the advantage derived from the use of a condenser depends only on the increased suddenness with which the current is stopped." In a later discussion of the same problem (*'Phil. Mag.'* vol. 2, pp. 280-285 (1901)), which for convenience may be referred to here, a different conclusion is, however, arrived at. Theoretical reasons are given why the condenser can offer no advantages beyond that

of causing a more sudden cessation of the primary current. The subject was verified experimentally, using special devices for interrupting the primary by firing part of it away with pistol or rifle bullets. In one of the experiments described, an Apps coil, with a mercury-oil break and condenser, gave only feeble brush discharges when the spark gap was 60 mm., while without the condenser good sparks were nearly always obtained when the primary was interrupted by a bullet fired from a service rifle.

In 1870 two papers were published in the 'Philosophical Transactions of the Royal Society.' The first is mainly mathematical, the result being applied to the determination of the stationary thermal condition of a sphere exposed to radiation from distant surrounding objects; the second, "On the Theory of Resonance," marks the beginning of that series of memoirs which ultimately was collected and extended in the treatise on "Sound." The importance of that work was at once recognised by no less an authority than Helmholtz, who, in a review of the first volume, wrote:—

"The author will merit in the highest degree the thanks of those who study Physics and Mathematics if he continues the work in the same manner in which he has begun it in the first volume The author has rendered it possible, by the very convenient systematic arrangement of the whole, for the most difficult problems of acoustics to be now studied with far greater ease than hitherto."

It is almost unnecessary to repeat that the feature which renders the two volumes so attractive to the reader, even if he be not specially interested in acoustics, consists in the method which, while illustrating general principles, are at the same time adapted to obtain numerical results in particular cases. This is very noticeable in the paper on Resonance, which forms the first of the series. In conservative vibrating systems of one degree of freedom there is an alternating interchange of potential and kinetic energy. Two constants enter into the mathematical expression of the energies, and once these are determined the natural period of the system is obtained in a simple manner. For air vibrations in cavernous spaces, the dimensions of which are small compared with the wave-length, and which communicate with the external atmosphere by small holes, the problem of determining the period had been solved by Helmholtz, but Rayleigh's method enabled him to find with equal facility expressions for the case where the communication with the external air is no longer by a mere hole, but by a neck of greater or less length. The solution, as has been pointed out, depends on the determination of certain constants. The potential energy is derived from the mechanical value of the compression when the kinetic energy is zero; it depends on the internal volume of the resonator and the compressibility of the gas. The kinetic energy is determined by a method which forms the chief novelty of the paper. The velocity of the air is, of course, greatest near the opening passage, and may be neglected at a short distance from either end of it. The specified condition that the

volume considered is small compared with the wave-length implies that the motion may be considered to be essentially that of an incompressible fluid. Taking these circumstances into account, it can be shown that the constant which is required is identical with what, in the theory of electricity, would be called the electric conductance of the passage supposed to be occupied by uniformly conducting matter. The exact calculation of this conductance presents generally great mathematical difficulties, but by certain assumptions two values, not differing much from each other, may be obtained, one of which gives too high and the other too low an estimate of the pitch.

In the last part of the paper the results obtained are tested by observation. For resonators with one circular aperture, Helmholtz had already obtained an equation agreeing in form with an experimental formula found by Sondhauss, but giving results differing by more than a semitone, or about 7 per cent. This difference would be increased still further if the thickness of the side of the vessel, neglected in the equations, were taken into account. In order to explain the discrepancy, the first question that arose was connected with the method employed to make the resonators speak. Sondhauss blew obliquely across the opening through a piece of pipe with flattened end, but Rayleigh points out several sources of error in this procedure. He was led in consequence to abandon the method of causing the resonator to speak by a stream of air, and to rely on other indications, such as the determination of the note of maximum resonance. This could be done in some cases to a quarter of a semitone by striking a note on the piano and listening to the resonance by means of short indiarubber tubes inserted into the ear and fixed to the resonator. The pitch belonging to small flasks with long necks could be determined by holding them close to the piano, when the resonant note causes a quivering of the body of the flask, easily perceptible by the fingers. With proper precautions in the conduct of the experiments, the theoretical formulæ were always confirmed with considerable accuracy.

After completing the paper, the main results of which have just been described, Rayleigh became acquainted with an experimental investigation of the subject which had been published a few months previously by Dr. Sondhauss in Poggendorff's '*Annalen*.' On the strength of his observations Dr. Sondhauss gave a formula for the pitch of resonators with cylindrical necks. This formula differed in some important respects from that deduced by theory, but in a communication to the '*Philosophical Magazine*,' vol. 40, p. 211 (1870), Rayleigh was able to show that his own rational equations fitted the facts even better than the formula of Dr. Sondhauss.

Several communications to the London Mathematical Society were evidently connected with the preparation of his Treatise on Sound. These deal with the vibrations of a gas contained within a rigid spherical envelope, the disturbances produced by a spherical obstacle in waves of sound, and some general theorems relating to vibrations. The last mentioned paper is of

particular interest, as it introduces for the first time the "Dissipative Function" into the general equations of dynamics; but it contains other important results such as "that an increase in the mass of any part of a vibrating system is attended by a prolongation of all the natural periods, or at any rate that no period can be diminished." The principle of reciprocity, particular cases of which had been discussed by previous writers, is considered in its most general aspect.

Rayleigh's attention having been drawn to an echo which returned the sound of a woman's voice with the pitch an octave higher, he was able to give the explanation, founded on his investigations relating to the effect on waves of obstacles small compared to the wave-length. The diverting power of such obstacles was found to vary inversely as the fourth part of the wave-length. The echo referred to was due to a plantation of fir-trees, the trunks and branches of which may be considered as obstacles satisfying the required conditions as regards dimensions. In the reflected or scattered sound, the octave supposed to be contained in the incident wave will be returned with an intensity relatively sixteen times stronger than the fundamental. It may therefore become the dominant note of the echo.

In the year 1877, '*Nature*' published a short article by Lord Rayleigh on "Absolute Pitch," which illustrates his singular power of tracing discrepancies to their source. To determine the pitch of a note an arrangement invented by Appunn had come into favour. A series of sixty-five harmonium reeds were tuned so that each when sounding together with its neighbour gave four beats per second. If the pitch of the first be such that the last is exactly the octave of the first, the lowest reed must emit a note of exactly 256 vibrations per second. Proper corrections being made for slight inaccuracies of tuning which reveal themselves by the number of beats between successive reeds being slightly greater or less than four, the arrangement was accepted as irreproachable, but when compared with König's standard a difference of nearly 1 per cent. was revealed. The difference was too large to be accounted for by errors of observation and seemed to indicate some defect in one of the methods employed. The fault lies with Appunn's instrument, but it is by no means obvious. All previous investigators had assumed that the pitch of each reed of the tonometer is the same whether it be sounding together with the reed above or with the reed below. For reasons given in the "Theory of Sound" the assumption is not justified, but there appears to be a mutual influence of the reeds, the sounds repelling each other. This would account for the higher value of Appunn's standard as compared with that of König. The same paper contains the description of a method of comparing directly the frequency of a tuning-fork with that of a pendulum clock. The method gave excellent results and confirmed König's standard.

By another interesting experiment described in the same year, an attempt was made to determine the amplitude of a sound wave in air which lies at the limit of audibility. A whistle was sounded by a constant blast of air so

that the work done per second on the air could be calculated. The necessary data are obtained by measuring the distance between the source of the sound and the point at which it ceases to be audible, and it was thus found that the sound of the whistle could be heard when its amplitude is less than a ten-millionth of a millimetre. On the strength of these experiments Lord Rayleigh expressed the opinion that a sound of the pitch of the whistle (about 2730 vibrations per second) would still be audible when the amplitude is reduced to a hundred-millionth of a millimetre. He confirmed this seventeen years later by an entirely different method, in which tuning-forks were used of frequencies between 256 and 512, the amplitude of the aerial vibration which is just audible being found to be about 5×10^{-9} cms., with a tendency to become less as the pitch rises.

In the five volumes of the collection of 'Scientific Papers,' a number of observations are discussed in nine papers having the title "Acoustical Phenomena." They are chiefly of an experimental character, and I shall have further occasion to refer to some of them, and more especially to those relating to the perception of the direction of sound. At the present stage it is sufficient to draw attention to one important fact brought out in the discussion of the "Æolian Harp" (vol. 2, p. 413).^{*} Previous to the publication of this paper, it had always been assumed that the vibrations of a stretched string sounding under the influence of wind took place in the direction of the wind. Observation, however, showed that this was not correct, the vibrations on the contrary taking place in a plane at right angles to the wind. Rayleigh makes no suggestion with regard to the origin of the forces which set the string in motion, but he found that the wind must be steady in order to maintain the vibration: "It is the irregularity, and not, as has been asserted, the insufficiency of the wind which prevents the satisfactory performance of the harp in the open air." These experiments are insufficiently known, and difficulties have consequently been felt in explaining that the loudness of the sound emitted by telegraph wires under the influence of wind bears no direct relation to the strength of the wind. In the second edition of his 'Treaty on Sound,' vol. 2, § 372, Rayleigh refers to Strouhal's empirical equation connecting the period of vibration with the diameter of the wire and its velocity relative to the air. This equation was based on experiments in which a vertical wire was made to revolve with uniform velocity about a parallel axis. On the assumption that the production of sound depends on the instability of vortex sheets, it was shown that Strouhal's formula may be derived from the theory of dimensions and may be generalized by introducing the coefficient of viscosity. To clear up outstanding questions, Rayleigh had already in 1896 expressed the desirability of extending the observations to liquids. This was actually accomplished by him in 1915, a pendulum free to move in one plane dipping into a vessel of water that could be made to rotate round a vertical axis (vol. 6, p. 300). No motion could be observed when the water flowed in the direction in which

^{*} Unless otherwise stated all references are to the 'Scientific Papers.'

the pendulum was free to oscillate, but it was set into vibrations when the motion of the water was at right angles to that direction. The results obtained were found to be in fair agreement with the theory.

While Rayleigh's work covered almost every branch of Physics, it is generally possible to trace in his consecutive publications the steps by means of which he was led from one problem to another. It would therefore be interesting to be able to fix his starting point. The great attention he paid during the first few years of his scientific activity to the problems of sound may have been due to a predilection for music which frequently accompanies mathematical ability. It probably was so in part; but Rayleigh's general method of attacking problems suggests an alternative explanation at any rate as a contributing influence. There were at the time many important questions in Optics demanding closer investigation, and their difficulties were of two kinds. One is common to all problems involving the origin and transmission of vibrations, the other is connected with the unknown constitution of the medium conveying light and the conditions regulating the different rates of transmission through transparent bodies. It was eminently consistent with Rayleigh's usual procedure to separate the difficulties, and to begin by investigating problems involving vibrations in cases where the mechanical conditions were known and definite.

It is therefore probable that from the beginning he intended to direct his attention to Optics, and in this connection it is of some interest to quote from a letter acknowledging the award of the Rumford Medal of the Royal Society in which he writes that his optical work "has been done perhaps more *con amore* than any other."

At the time when the medium conveying light was supposed to possess the properties of an elastic solid, there was a fundamental question in Optics on which two opposite views were held. Is the direction of the vibration in a polarized ray parallel or at right angles to the plane of polarization? Rayleigh's early papers on Optics endeavoured to elucidate this point from several sides. The first of them deals with the polarization and colour of the light from the sky. Tyndall's experiments had shown that the blue light scattered from small particles was polarized in a direction perpendicular to that of the incident beam. As regards colour, Rayleigh showed that its explanation was simple, for it followed from the principle of dimensions alone that, when the particles were small compared with the wave-length of the incident light, the intensity of the scattered beam must vary inversely as the fourth power of the wave-length. Before working out the theory, the actual prismatic composition of the blue of the sky, as compared with sunlight, was examined experimentally, and found to be in good agreement with the theoretical laws.

The more detailed investigation involving the direction of the vibration depends on the assumption that the scattering particles act in virtue of their greater density by loading the aether so as to increase its inertia without altering its resistance to distortion. The result arrived at shows that the

light should be completely polarized at right angles to the incident beam, and that in order to make theory agree with observation the direction of vibration must be at right angles to the plane of polarization. A further paper on the same subject extends the investigation, and considers the case where the scattering particles differ in rigidity as well as in density from the surrounding medium; the conclusion is arrived at that if both properties vary there is no direction in the plane perpendicular to an incident ray in which there is complete polarization. If there be such a direction—and observation shows that there is—the particles must act either entirely by a change of inertia or entirely by a change of rigidity. In the latter case, however, if the incident beam be polarized, the scattered light should not only vanish in two directions perpendicular to the original ray, but also in four other directions in the plane containing the ray and the direction of vibration, and equally inclined to both. No such polarization is observed, and we are therefore forced to conclude that the particles act through an increase of inertia and do not affect torsional rigidity. In a further communication published in 1881, the subject is treated from the point of view of the electromagnetic theory. Here, again, we have two alternatives, according as the particles act in virtue of introducing variations of electrostatic capacity or of magnetic induction. The second case is excluded for the same reasons that preclude the assumption of an alteration of rigidity in the elastic solid theory. The subject is pushed further in an important respect. All previous results depended on the neglect of powers higher than the first in the supposed alteration of the properties of the medium. In order to find the effect of higher powers, the shape of the particles has to be taken into account. The problem is solved for spherical obstacles, and it is found that the second approximation still maintains one direction of complete polarization, but turns it away from the direction in which the light proceeds. Experiments confirmed this in so far as the maximum polarization could be shown to alter in the manner indicated by theory, but complete polarization was not obtained. This failure is accounted for by the irregularity in the size of the particles, the direction of complete polarization depending on the size. It is further pointed out that the mathematical result only applies to spherical obstacles; with elongated bodies it might be different, and this remark is of importance in connection with the recent investigations of the present Lord Rayleigh.

In a later paper published in 1899 further results of the greatest importance are obtained. The total light scattered by a number of small particles is easily calculated, and the scattering in the direction of the original wave-front is shown to lead to a retardation of phase and therefore determines the refractive index of the medium. Hence a relation may be found between the gradual diminution of intensity, the number of effective particles, and the refractive index.

In these investigations the particles have been supposed to act only in virtue of their increased density or inductive capacity. Modern theories assign the cause of the retardation of phase to the forced vibrations of the

molecule. The effect then depends on the free periods, and, therefore, involves dispersion as well as refraction; but there is no difficulty in showing that the general relation deduced by Rayleigh holds also in this case. The question now obtrudes itself as to whether the scattering particles in the atmosphere are molecules, or whether extraneous matter in the form of dust is the active agent. Using Maxwell's estimate for the number of molecules of air under standard conditions, and Bouguer's value for the absorbing effect of clear air, it was found that about one-third of the total scattering was due to air molecules. A much closer agreement is obtained when more accurate figures are substituted for those available at the time Rayleigh's paper was published. Maxwell under-estimated the number of molecules in a gas, and we now possess accurate measurements for the transparency of air at Washington and Mount Wilson. The average difference between the coefficient of extinction observed on clear days at Mount Wilson and that calculated from the scattering by the molecules of air in different parts of the spectrum is less than 0.5 per cent., and would be practically zero if a small region in the red (probably affected by ordinary absorption) be excluded. It may, indeed, be said that as good a measure of the number of molecules in a gas may be obtained from its refractive index and transparency as by any other method.

Rayleigh's paper of 1881 is the first which is based on Maxwell's theory of light. Up to that date, the formulæ of the elastic solid theory, involving a purely mechanical view of the density and rigidity of the æther, was adopted, and difficulties had to be considered which do not appear in the electromagnetic theory. It may be said in explanation that Maxwell had not specially considered the problem of reflexion. That the surface conditions in the electromagnetic problem lead to expressions which are in better accordance with optical experiments than the elastic solid theory was first pointed out by Helmholtz in 1870, but the brief reference, relegated to a footnote in a long paper, did not attract attention. The mathematical investigations by Glazebrook and Fitzgerald appeared in 1879 and 1880 respectively, while Rayleigh's papers, in which some reference to Maxwell's theory might have been expected, were published in 1871. These papers, written mainly for the purpose of determining the direction of the disturbance in a ray of light, may, as regards their main purpose, perhaps be now considered to have only historical interest; but not entirely so, because the strictly scientific discussion of the propagation of waves in an elastic medium, with well-defined mechanical properties, has applications outside the domain of Optics, and the comparison of the conditions prevailing in an elastic body with that of the imaginary medium conveying electromagnetic disturbances, has still a valuable educational importance. Even if this be not admitted, the historical growth of the present theory of light justifies a brief account of the many contradictions with which the elastic solid theory of light was confronted during the middle of last century. These contradictions were well brought out in Rayleigh's papers, which contain an

eminently clear and fair account of the work of previous investigators. We have already seen that his treatment of the problem of the scattering of light by small particles had led him to the conclusion that the effects of refraction must operate through changes of inertia and not of rigidity. This view had to be tested in other branches of Optics. In double refraction, the same periodic force must suffer a different reaction according to the direction of the force; and it had been assumed by Fresnel and his followers that it is the elasticity that varies. Rayleigh rejects that view on the ground of his previous work and of other fatal objections, which were discussed more fully in a subsequent paper: "We have, then, to consider the question," he asks: "Can double refraction be explained if the statistical properties of the æther are independent of associated matter? Can we suppose that the density within a crystal is a function of the direction of vibration? I answer: Yes. The absurdity is apparent only, and disappears on more attentive examination." He continues his argument by considering—as illustration—an elongated body, such as an ellipsoid, which in the extreme case becomes a circular disc of inconsiderable thickness. If such a disc be suspended in a frictionless medium so that it can be made to perform oscillations in different directions, the medium will have no effect if the displacement be parallel to the plane of the disc. But if it be perpendicular to that plane, the motion of the disc involves a motion of the medium, and the inertia of the moving mass is increased. In a footnote, added in 1899, it is pointed out that Rankine had already in 1851 suggested an inertia different in different directions. Following up this idea, Rayleigh formulated a theory of double refraction, which leads to a wave-surface slightly differing from that of Fresnel. At the time the paper was written, no measurements were available of sufficient accuracy to decide between the two theories; but, shortly after its appearance, Sir George Stokes supplied the deficiency, and gave experimental evidence, which decided the point in favour of Fresnel's wave-surface. This was confirmed in a more complete investigation by Glazebrook.

The reflexion of light from transparent matter was investigated by Fresnel, but it was Green, who, in 1837, first gave a theory based on dynamical principles. A critical discussion of the work of Green, McCullagh, Neumann, and others will be found in Rayleigh's paper published in 1871. When the vibrations are at right angles to the plane of incidence, *i.e.*, parallel to the surface of separation, the mathematical investigation is simple. Assuming the rigidity to be independent of the medium, the amplitude of the reflected wave for unit amplitude of the incident wave was found by Fresnel to be expressed by $\sin(i-r)/\sin(i+r)$, where i denotes the angle of incidence and r that of refraction. If the densities, on the other hand, are supposed to be the same, as in the theories of Neumann and McCullagh, the same amplitude is found to be $\tan(i-r)/\tan(i+r)$. The former expression correctly represents the reflected amplitude for light polarized at right angles to the plane of incidence. Hence, according to Fresnel, the displacements are at right

angles to the plane of polarization, while, according to McCullagh and Neumann, they are parallel to it. But, to complete the theories, it would have to be shown that, for displacements in the plane of incidence, Fresnel's theory would lead to the tangent formula and Neumann's to the sine formula. Their respective authors claimed to have done so, but they obtained their result only by neglecting certain surface conditions which can only be satisfied by introducing surface waves which, though insensible at finite distances, must necessarily affect the amplitude of the reflected wave. Retaining Fresnel's assumption, Green obtained an equation differing from the tangent formula, the discrepancy being small, except near the polarizing angle. Assuming, on the contrary, that the densities are equal, we are led—as Rayleigh shows—to an impossible result, for it would follow that there should be two polarizing angles whenever the difference of refrangibility is small. What interests us here is that he already appreciated in these early papers the close connexion between molecular scattering and the problems of reflexion and refraction, this double polarizing angle having been anticipated by him from his previous investigations, though the mathematical process employed in the treatment of scattering was very different.

It is not necessary to pursue the subject further, because Fresnel's formulæ are easily obtained on the electromagnetic theory, if we treat the media as homogeneous and refraction as being due to differences in inductive capacity. The elliptic polarization accompanying deviations from the tangent formula near the polarizing angle must be due to other causes, among which the oscillatory properties of the molecules, which account for dispersion, demand consideration. There is good evidence that Rayleigh recognised this, for in his treatment of the reflexion and refraction of light by intensely opaque matter, he discusses the effects of anomalous dispersion, and points out that in the increase of refraction on the red side of an absorption band and in its diminution on the violet side, "an analogy may be traced with the repulsion between two periods which frequently occurs in vibrating systems." In a footnote, added in 1899, attention is drawn to an examination question set by Maxwell in the Mathematical Tripos for 1869, showing that he had anticipated Sellmeyer in explaining anomalous dispersion by the reactions of the internal forces of the molecules. As regards the deviations from Fresnel's law, we shall see how at a subsequent stage Rayleigh was led to examine the effects of surface contamination.

The problem of reflexion cannot be completely understood without examining the conditions which are necessary in order that there should be a reflected ray at all. The ordinary theory assumes a definite boundary at which the properties of the medium change abruptly. If the transition is gradual, as in the case of an atmosphere in which the density varies slowly, there is no reflexion. The thinness of the transition layer necessary for the production of reflexion may be expected to have some relation to the wave-length. The problem (vol. 1, p. 460) is treated by Rayleigh in a

simple imaginary case which will assist the student in forming a clear view of the general process.

In the first three years of his scientific activity, the starting point of Rayleigh's investigations was mainly a theoretical problem, and though the clearing up of obscurities or the discussion of difficulties were nearly always supplemented by well-designed experiments, these did not call for any considerable manipulative skill. It is otherwise with his efforts, now to be mentioned, to reproduce optical gratings by photographic methods. That his attention should be directed to this subject at an early stage in his career is of special interest, because this investigation, which at first appeared to have only a practical value, led to a general discussion of the powers of optical appliances, and resulted in the discovery of laws having fundamental importance. Gratings, at the time, were ruled on glass; they were expensive, and differed much in quality. Rayleigh soon gave up the idea which had originally occurred to him of constructing one "on a comparatively large scale and gradually reduce it by the lens and camera to the required fineness." He adopted what he considered the better method by taking a good grating and copying it in the way transparencies for the lantern are printed from negatives. Dry plates, which were then a novelty, were used, and had to be prepared by himself. The reader must be referred to the original papers for a description of the various methods employed, the precautions taken, and the discussion of their relative merits. He will be impressed by the great experimental skill displayed in achieving the success which was soon obtained. The gratings were tested by accurate optical methods, and many of the copies proved to be not inferior in their behaviour to the originals. The investigation led to a closer examination of the theory of gratings. This is simple enough if gratings are treated as made up of a series of openings separated by opaque spaces, but the assumption rarely corresponds to reality, and hence the intensity of light in the spectra of different orders is not, as a rule, what we should expect from the consideration of an equidistant series of openings. Thus it may be found that one of the lateral spectra is stronger than the central image. In most gratings, indeed, what is considered as the opaque part acts merely in retarding the phase of the vibration. "If the grating were composed of equal alternate parts, both alike transparent, but giving a relative retardation of half a wave-length, it is evident that the central image would be entirely extinguished, while the first spectrum would be four times as bright as if the alternate parts were opaque. If it were possible to introduce at every part of the aperture of the grating an arbitrary retardation, *all* the light might be concentrated in any desired spectrum" (vol. 1, p. 215).

The third of four papers on the subject was published in the 'Philosophical Magazine' (1874), and establishes the fundamental theorem for the resolving power of gratings. If a close double line, differing in wave-length by $\delta\lambda$, can just be recognised as such, the resolving power, *i.e.*, the ratio of their

wave-length to their interval as defined by the ratio $\lambda/\delta\lambda$, is shown to be determined by the total number of lines on the ruled surface multiplied by the order of the spectrum. The importance of this theorem lies in the fact that it is not the closeness of the lines but their total number which is effective.

It is convenient to discuss the further theory of gratings in connexion with the general question of the resolving power of optical instruments, which is treated with characteristic thoroughness in a paper, "Investigations in Optics, with Special Reference to the Spectroscope," published in four parts in the 'Philosophical Magazine,' during 1879 and 1880. There is a limit to the resolving power of all optical instruments, owing to the finite length of waves of light. In the case of telescopes, their power of resolving double stars had naturally received the attention of astronomers, and Airy had supplied the mathematical investigation which determines the image of a luminous point formed by a lens. This image is known to consist of a central disc surrounded by rings gradually diminishing in intensity. In 1872, Rayleigh had already pointed out that the diameter of the central image could be reduced, and therefore the resolving power increased, by blocking out the central portion of the lens. Such increase involves, of course, a loss of brilliancy, but this might be advantageous where there is superabundance of light, as in investigations dealing with the sun. The paper was read before the Royal Astronomical Society, Rayleigh's object being to draw the attention of astronomers to a method enabling an observer to protect his eyes against excessive radiation, while at the same time improving the optical efficiency of the telescope. The method is, however, open to the objection that it is not only the eye that ought to be protected but the lens of the telescope, which, when exposed to sunlight, is distorted by unequal expansion due to the absorbed radiation; the present practice favours a partial silvering of the outer surface of the lens for telescopes of very high resolving powers. With smaller powers, when the effect of radiation on the shape of the lens is negligible, Rayleigh's method might still be worth trying.

In the application of the wave theory to the optical powers of prisms and gratings, Rayleigh breaks entirely new ground. If homogeneous light be examined after passage through a prism spectroscope, the width of the image of the slit treated according to the laws of geometrical Optics depends on the orientation of the prism. With equal focal length of collimator and telescope the width of the image is equal to that of the slit only when the prism is in a position of minimum deviation, becoming smaller if the prism be turned in one direction, and larger if turned the opposite way; the dispersion alters at the same time, and hence with wide slits the purity of the spectrum depends on the position of the prism. While attention had been paid to such considerations, it is surprising that no one should have recognised that with narrow slits the laws of geometrical Optics no longer regulate the size of the image, but that—as in the case of telescopes—the purity obtainable is

ultimately limited by the wave-length. Whether viewed through a prism or a grating the width of the central image of a slit illuminated by homogeneous light depends entirely on the difference in the phases of vibration of the two extreme rays. If that difference be equal to a wave-length, the amplitude is zero, and at this point the central image may be said to terminate. It follows in the words of Rayleigh (vol. 1, p. 217), that "if a grating and a prism have the same horizontal aperture and dispersion, they will have equal resolving powers on the spectrum; the greater dispersion is the only cause of the superiority on the diffraction spectra of high order."

In order to express in a mathematical form the limits of resolving power some adequate convention is necessary to define the point at which a double line may be recognised as such. When the principal maximum of the image of one line falls on the first minimum of the other, the combined image has two maxima separated by a minimum, the brightness of which is 0.81 that of the brightness of the maxima. An experienced observer will then have at any rate a strong impression that he is looking at a double line. Taking this as his standard, Rayleigh, as already mentioned, had shown that the resolving power of a grating is equal to the product obtained by multiplying the total number of lines with the order of the spectrum. In the case of prisms the power depends on the dispersive power of the material used and is otherwise proportional to the effective thickness of the material traversed by the extreme ray. "That the resolving power of a prismatic spectroscope of given dispersive material is proportional to the total thickness used, without regard to the number of angles or setting of the prisms, is a most important, perhaps the most important, proposition in connexion with this subject. Hitherto in descriptions of spectroscopes far too much stress has been laid upon the amount of dispersion produced by the prisms; but this element by itself tells nothing of the power of the instrument" (vol. 1, p. 426).

One further point remains to be noted. In order that the full resolving power may be realised, it is necessary that the magnifying power of the optical arrangement should be sufficient to allow the whole of the emergent beam to enter the eye. When the magnifying power is further increased, though there is no loss of resolving power, there is loss of illumination. Nevertheless there is generally an advantage in narrowing the beam until its width is one-third or even a quarter of the diameter of the pupil, on account of the imperfections of the lens of the eye. Rayleigh further discusses the effects of aberrations in optical instruments, the accuracy required in optical surfaces, and concludes his now classical paper by some remarks on the design of spectroscopes. "The general results of the discussion would seem to be in favour of a spectroscope with simple glass prisms of such angle that the reflected light is wholly polarized, the number of prisms being increased up to the point at which mechanical difficulties begin to interfere" (vol. 1, p. 457).

A problem which has important applications in several branches of Physics is solved in a communication to the '*Philosophical Magazine*' (1880), under

the title, "On the Resultant of a Large Number of Vibrations of the same Pitch and of Arbitrary Phase." If we consider a space traversed in all directions by radiations of the same period, the question as to the magnitude of the resultant vibration at any one point had been raised by Verdet, who arrived at the conclusion that the resultant of n vibrations of unit amplitude and arbitrary phase approaches the value $\sqrt{n}$ when n is very great. Rayleigh had already shown in 1871 that Verdet's reasoning is incorrect, and in the more complete investigation an expression is obtained for the probability that the magnitude of the resultant lies between any assigned limits. Though the intensity and phase of the resultant is shown to be indefinite, the expectancy of the intensity, *i.e.*, the average intensity in a great number of cases, is found to be equal to the product of the number of combined vibrations and the common intensity.

A question very different at first sight can be shown to be subject to the same mathematical conditions. When a number of detached events, such as earthquake shocks, is treated by the harmonic analysis, the time being the independent variable, the magnitude of the amplitude to be expected for any one period depends on the magnitude of each event exactly in the same manner as in Rayleigh's problem. Another example was supplied by Karl Pearson, who, in a letter to 'Nature' (vol. 72, p. 294), put the following question: "A man starts from a point O and walks l yards in a straight line; he then turns through any angle whatever and walks another l yards in a second straight line. He repeats the process n times. I require the probability that after these n stretches he is at a distance between r and $r+dr$ from his starting point, O." Lord Rayleigh could give the answer at once (vol. 5, p. 256), for it was practically the same problem as that of the composition of n iso-periodic vibrations of unit amplitude and arbitrary phase. Further applications of the fundamental proposition, including its extension to three dimensions were made in papers (vol. 6, p. 565; vol. 6, p. 604) published in the last two years of his life.

The survey of this period of Rayleigh's activity would be incomplete if his important contributions to Hydrodynamics were omitted. The author's index to Lamb's treatise contains sixty references to Rayleigh's papers, and of these more than half were published before 1880. We may note more especially his clear discussion of the "vena contracta" and the "solitary wave." An appreciation of this work dealing with the science of Hydrodynamics from the pen of Prof. Lamb will be quoted further on.

In the account which has been given, and which is by no means exhaustive, of the first ten years of Lord Rayleigh's scientific work, nearly every branch of Physics has been touched upon; yet, as has already been pointed out, the subjects treated are not a mere collection of enquiries which flit haphazard from one subject to another. Occasionally a casual observation or an obscure passage met in the course of reading suggested some point that wanted elucidating, but taken as a whole, the width of range was consequential on the generality of his outlook. In a sense it was more apparent than real.

For to one who primarily considered the fundamental principles on which the science of Physics was then built, and who was constantly on the look-out for applications of these principles, the division of Physics into departments could have but little meaning. There would be no difficulty, were it necessary, to trace the connecting threads which run through the greater part of Rayleigh's theoretical writings and experimental researches. But this might leave a false impression, for no one was more apt than Lord Rayleigh to utilise the opportunities that came to him from the circumstances of his life, or the discharge of his duties, in finding new directions of enquiry. The Cavendish Professorship, the Secretaryship of the Royal Society, the Presidency of the Royal Society all afforded such opportunities, which were used to the best advantage. To appreciate his power of work and devotion to science, it must be remembered that the first period of his career was interrupted by at least one serious illness, and that he had to fit up his own laboratory and carry out single-handed the manual work and often the construction of apparatus required in his experiments.

When Clerk Maxwell died on November 5th, 1879, Lord Rayleigh, by general consent, was invited to succeed him as head of the Cavendish Laboratory, and his acceptance of the post was welcomed by all who were anxious for the future of Physics at Cambridge. He was elected on December 12th, 1879, and entered on his duties at the beginning of the following Lent Term.

The building of the Cavendish Laboratory originated in a report of the Physical Science Syndicate of Cambridge University, which recommended the establishment of a Professor and Demonstrator in Experimental Physics, estimating the cost of a suitable building to be £6,300 inclusive of the apparatus required. The scheme threatened to fail for want of financial support, when the seventh Duke of Devonshire, then Chancellor of the University, offered to provide the necessary funds. After the plans had been drawn out, it was found that the lowest estimate for the building was £8,450, and the Duke generously offered to defray all expenses, including the sum required for equipment. The laboratory, opened in 1874, was thus provided with apparatus necessary for lecture demonstrations and a number of instruments in common use for experimental work. Maxwell thought the Duke "had done enough"* and a year or two later expressed the opinion that the gift should be considered as completed.

The original equipment being inadequate, Lord Rayleigh found it necessary, partly for the purposes of research and partly for the ordinary instruction of laboratory practice, to raise a further sum of money. He contributed £500 himself, and the Duke of Devonshire added another £500 to his previous gift. The total amount subscribed was about £1,500.

Rayleigh gave considerable thought to the organisation of the laboratory as a place of instruction and research, and consulted a few friends who were

* These were the words used in a conversation which remains firmly fixed in my memory.—A. S.

acquainted with similar laboratories in other Universities. But one idea to which he attached importance and which was entirely his own, was to identify the laboratory with some research planned on an extensive scale, so that a common interest might unite a number of men sharing in the work. As a suitable subject he selected the re-determination of electrical standards, and tried to obtain volunteer workers to take part in it. In this he was not altogether successful; partly because the number of sufficiently advanced students was not great, and perhaps also on account of the natural wish of a beginner to try his hand at a problem in which he could show his individual powers. Mr. Horace Darwin, who assisted in the work in its preliminary stages, was prevented from continuing by other occupations. I was then engaged in spectroscopic investigations, but had sufficient faith in the advantage of the general scheme and the importance of the special problem to abandon for a time my own work.

There was a special reason why the determination of the Ohm should be carried out at Cambridge. Clerk Maxwell was closely connected with the experiments on the C.G.S. unit of resistance carried out by a Committee of the British Association at King's College, London, in 1863, and the apparatus based on a method devised by Lord Kelvin was in the custody of the Cavendish Laboratory. Some doubts had been thrown on the accuracy of the experiments. Rowland had found that the British Association unit was 1 per cent. too small, while, according to Kohlrausch, it was 2 per cent. too large. It seemed important, therefore, to repeat the experiment.

The method used consists in observing the deflection of a magnet suspended at the centre of a coil which is made to rotate about a vertical axis. Its accuracy depends on a correct estimate of the self-induction and the dimensions of the coil. Though the construction of a new apparatus of larger size was contemplated from the first it was thought desirable to repeat the experiment with the original coil and to introduce only modifications in the arrangements. Without entering into a discussion of the difficulties that were encountered both on the observational and theoretical side, the stroboscopic method for regulating and determining the speed of rotation of the coil deserves to be noticed. On the axis of the instrument a stout card was mounted divided into concentric circles of black and white teeth of equal width. There were five circles containing 60, 32, 24, 20 and 16 teeth respectively. This disc was observed from a distance through a telescope, and an arrangement for affording an intermittent view with the help of two plates of metal, one of which was fixed and the other attached to an electrically driven tuning fork. The two plates were perforated with slits parallel to the prongs of the fork, so that a view of the revolving disc could only be obtained twice in each complete vibration of the fork. The teeth of the disc appear to be at rest if in the interval between two sights one of the teeth has taken the place of another. By means of the various circles a variety of speeds could thus be brought under observation. The motive power was derived from a water-motor and conveyed to the spinning coil

through a string fastened at a convenient distance below the vibrating fork. The observer by applying a slight friction to the string through the hand could maintain a constant speed, increasing or diminishing the friction according as the teeth of the disc were seen to be displaced in one or the other direction. This method designed by Lord Rayleigh proved very successful and during the whole course of the experiments he himself took charge of that part of it. To get a correct value of the speed it is necessary to know the frequency of the fork. The frequency of the standard was obtained by comparing it directly with a pendulum clock according to a method previously used by Lord Rayleigh and already referred to.

One of the minor troubles that for a time interrupted the smooth progress of the experiment was the behaviour of the suspended magnet, which, when the coil was spinning with open circuit, seemed occasionally jerked suddenly to one side. The investigation of the source of disturbance, which was traced to mechanical tremors, was used by Lord Rayleigh to illustrate an important hydrodynamical effect. It is known that a flat body tends to set itself across the direction of any steady current of the fluid in which it is immersed, and the effect may be expected to show itself also when the current is alternating. If the box containing the magnet and mirror be subject to mechanical vibration, the air in the box will move past the mirror and probably execute several vibrations, the effect of which will be additive. The mirror will, therefore, be subject to a twisting force, tending to set it at right angles to the direction of vibration.

A striking experiment in support of the explanation is described by Lord Rayleigh as follows: "A small disc of paper, about the size of a sixpence, was hung by a fine silk fibre across the mouth of a resonator of pitch 128. When a sound of this pitch is excited in the neighbourhood, there is a powerful rush of air in and out of the resonator, and the disc sets itself promptly across the passage." An instrument capable of measuring the intensity of aerial vibrations, based on this principle, was subsequently designed by Rayleigh (vol. 2, p. 90).

The final result of the investigation on the unit of resistance, conducted with the original apparatus, was that the Ohm, as determined by the British Association Committee, is 0.9893 of a true Ohm, and therefore over 1 per cent too small. The error is in the same direction, but even greater than that found by Rowland.

The research was continued with a new apparatus increased in size in the ratio of 3 : 2, and carefully wound so as to avoid uncertainties in the mean diameter of the winding, which had been troublesome in the previous experiments. The result now gave a value of 0.98651 true Ohms for the B.A. unit, or slightly smaller than the preliminary result.

Mrs. Sidgwick, who from the first assisted in the experiments, took a more responsible share in the later observations, and her name appears as joint author in most of the subsequent work on electrical standards. The time had

arrived when the accurate measurement of resistance, current, and electromotive force became a matter of great industrial importance, which rendered the continuance of the work imperative. A discussion of the relative merits of different methods of determining the Ohm which appeared in the 'Philosophical Magazine' (1882) had led Lord Rayleigh to the conclusion that the one associated with the name of Lorenz, of Copenhagen, was that which promised the best results. With an important improvement, the method was applied and led to a result giving 0.98677 Ohm for the British Association unit, in close agreement with the value obtained with the revolving coil. The general adoption of the Ohm as a unit of resistance was delayed by the favour shown in some quarters to the practical standard of Dr. Werner Siemens. This standard, which could be reproduced without great difficulty when no very high accuracy is required, consists in the resistance of a column of mercury, 1 m. long and 1 sq. mm. in section. This unit was known to be smaller than the Ohm by about 4.5 per cent., and it was important to establish the relationship more accurately. The actual unit in use could be compared with the standard Ohm, but it remained to be shown that it conformed sufficiently with its definition, and for this purpose it was necessary to investigate independently the specific resistance of pure mercury. This was done by Lord Rayleigh and Mrs. Sidgwick.

There remained the important question of establishing a standard method to enable the intensity of a current to be determined in absolute units. The unit current is defined by the magnetic field it establishes, and this field may be measured by its effect either on a suspended magnet or on a suspended coil through which a current passes. For reasons given in the paper, 'Scientific Papers,' vol. 2, p. 278, describing the results, Lord Rayleigh, who was again assisted by Mrs. Sidgwick, chose the second alternative. The ultimate object of the investigation was to enable observers to measure currents in absolute units with appliances that are generally available. Current balances are not suitable for the purpose; even if they can be obtained commercially—like those designed by Kelvin—their indications ultimately depend on the comparison with some standard instrument. It was desirable therefore to connect the results obtained with a standard balance with some laboratory method which is easily applied. Any commercial instrument can then be tested and its errors detected. The electrolytic effect of a current gives us a convenient and effective means of supplying the want. If it be known how much silver is deposited by unit current in a given time, observers may, with apparatus in common use, conduct any experiment in which the intensity of a current is required in absolute measure. The current balance designed by Lord Rayleigh possessed many novel features which all tended to increase the accuracy of the result. The difficulties encountered in pushing the limits of reliability of the silver voltameter to a point comparable with that of the current balance were successfully overcome, and the instructions supplied should enable all competent observers to measure their current to less than one part in a

thousand. In laboratories specially devoted to accurate measurement, a considerably higher accuracy has since been obtained.

The silver voltameter has a great disadvantage due to the time that is necessary to obtain deposits which can be weighed with sufficient accuracy. Currents of the order of one ampère require not less than half an hour to accumulate sufficient silver. It is therefore important to have an alternative method which is more rapid. An electric cell of known electromotive force could supply the deficiency, but when these experiments were conducted, no cell that could be relied upon was known. The most promising one was that constructed by Latimer Clark, depending on the electromotive force between pure mercury and zinc. Before it could be generally accepted as a standard, it was necessary to test its permanence, and the conditions under which cells set up by different persons could be relied upon to give identical results. Lord Rayleigh and Mrs. Sidgwick undertook this laborious work and finally carried it to a successful conclusion. When the highest accuracy is required, the somewhat large temperature coefficient of the electromotive force is a disadvantage, and the Weston cell, in which cadmium is used in the place of zinc, is now more generally adopted.

To complete the investigation of standard measurements of electric currents, there remained still one method which it was desirable to examine. A current passing through a helix establishes a magnetic field in its interior, the strength of which, in terms of the dimensions of the helix, can be expressed in mathematical form with sufficient accuracy. According to Faraday's discovery, this force will turn the plane of polarization of light when passing through refracting media such as glass, or bisulphide carbon. The latter substance may be obtained with sufficient purity, and it seemed desirable, therefore, to determine the angle through which, for unit magnetic force, a given length of the liquid would turn the plane of polarization. The research was carried through with the usual care and attention to relevant detail, but inherent disadvantages prevent the method from entering into competition with others that are more easily applied.

When Lord Rayleigh took over the Cavendish Professorship, the number of students was small, and there was little in the way of systematic instruction in laboratory practice. But the need for such instruction was growing, mainly in consequence of the increasing importance of the practical examination in the Natural Science Tripos. Courses were accordingly organised by the newly-appointed demonstrators, R. T. Glazebrook and W. N. Shaw. A greater number of advanced students also soon entered the laboratory, where they received encouragement and assistance from the Professor. His desire to bring all workers into contact with each other has already been referred to in connexion with the attempt to organise a joint research. The common afternoon tea, introduced by him, was an innovation which may appear to be trivial, but the custom, which affords opportunities for informal discussion of scientific matters and encourages friendly personal intercourse, has been copied in many laboratories, and has

served its object so well that its origin deserves to be placed on record. In connexion with the general policy adopted in the conduct of the laboratory, it should also be recalled that soon after his appointment Lord Rayleigh gave authority to admit women students on the same terms as men.

The room in which the common half-hour was spent in the afternoon contained appliances used by Lord Rayleigh in his many subsidiary investigations. Those who frequented the laboratory at the time will remember a number of roughly constructed but efficient optical devices, and the apparatus for studying the electrical influence on water jets. The investigations for which these appliances were constructed were generally connected with some previous work, and intended to clear up some remaining questions that required illustrating or elucidating. The conditions under which water breaks into drops, more especially, was a favourite study to which Lord Rayleigh frequently returned.

The introductory sentence of the first paper he published on the subject in 1879 (vol. 1, p. 361), expresses the origin of the interest he took in this subject: "Many, it may even be said most, of the still unexplained phenomena of Acoustics are connected with the instability of jets of fluid."

In this paper it is shown that there are two causes which may lead to instability in a cylindrical jet of fluid. One of these is dependent on surface tension, while the other is dynamical. If the fluid as it escapes through a circular orifice be subject to a slight periodic disturbance, such as may be caused by a tremor, the diameter of the jet contracts and expands alternately, so that the outline of the jet takes a wave-like form. The change of surface tension which then comes into play may either tend to increase or to diminish the disturbance. In the former case, the motion becomes unstable, and the jet loses its continuity. Instability will thus set in when—on the average—the disturbance diminishes the surface, for surface tension will then tend to make it smaller still, and therefore increase the effect of the disturbance. The mathematical investigation leads to the conclusion that the jet is unstable when the wave-length of the disturbance (*i.e.*, the period of the tremor multiplied by the velocity of the jet) is greater than the circumference of its cross-section. The wave-length which leads most rapidly to the disintegration of the jet is about 4·5 times as great as its diameter, or about one and a half times the wave-length at which instability first sets in. The subject is pursued in a number of papers, the later ones taking account of viscosity, and from the many instructive experiments arising out of it we may select those referring to the well-known electrical influence on jets as being of special interest. A vertical jet, not subject to any electrical influences, resolves itself into drops which are widely scattered before reaching the summit of their trajectories. When a feebly electrified body is then brought into the neighbourhood of the jet, it undergoes a remarkable transformation, and appears to become coherent. Rayleigh showed that the scattering is due to the rebound of the drops after mutual collisions, which must necessarily occur. In an

electrified field the drops, owing to electrostatic induction, attract each other. In consequence of this attraction, a collision between two drops leads not to a rebound but to a fusion, and hence the scattering is prevented. The exact manner in which fusion takes place has been the subject of some discussion, but adverting to alternative explanations Rayleigh, after some hesitation (vol. 2, p. 117), returns to his original conclusion of the fusion being assisted by the condenser action between the drops (vol. 4, p. 422). The experiment only succeeds when the electric forces are small, because as each drop carries away a charge from the main stream, mutual repulsion will overbalance the attraction if the charges are sufficiently great, and the scattering will consequently increase. When the subject was further examined, it was found that certain substances, such as milk, containing greasy matter, when mixed with water prevent the scattering, the jet reaching the summit in an unbroken stream, and interesting effects were observed when two independent jets were made to collide. The papers dealing with this subject were soon followed by one in which Laplace's theory of Capillarity was improved in an important particular relating to the intense molecular pressure inside solid and liquid bodies.

The second, or dynamical cause, which may produce instability, operates when the jet and surrounding medium have similar properties, so that the effects of surface tension become negligible. Such is the case when a jet of air or some other gas is projected into the atmosphere. The subject was studied by Rayleigh, more especially in connexion with flames sensitive to sound, and his investigation supplied important contributions both on the experimental and theoretical side.

Almost from the beginning of his scientific career, the theory of colour perception attracted Rayleigh's attention. As early as 1871, he communicated to '*Nature*' a note on colour vision. It was based on a repetition of Maxwell's experiments, in which colours were combined and matched by using coloured papers attached to and forming sections of a rapidly revolving disc. Rayleigh contributed some pertinent comments on the bearing of the experiments on the theory of trichromic vision. The great surprise to a novice, who begins to study the superposition of physiological colour sensations (as contrasted with the mixture of paints), is the artificial production of yellow by the combination of red and green. To observe the effect in its full brilliancy, pure spectral colours must be used. When these are not available, Rayleigh recommends an alkaline solution of litmus, which absorbs the yellow and orange, with the addition of chromate of potash, which removes the blue and bluish-green. If the relative proportions of the two substances be properly adjusted, a compound yellow may be obtained. In a further note to '*Nature*' (vol. 1, p. 542), an apparatus is described which enables an observer to determine the proportion in which the spectral red and green must be combined to match a pure yellow. A remarkable peculiarity, which affects some persons and appears to be hereditary, was thus discovered. While out of twenty-three male observers,

sixteen obtained results that were consistent with each other, five, of whom three were brothers, required twice as much green to convert red into yellow. The remaining two matched the yellow with less green than the sixteen, who may be supposed to have normal sight. The colour sensation of all women who submitted themselves to the test was normal. It seems highly desirable to secure further statistics on this point. The only attempt made to extend the observations is described by myself in the 'Proceedings of the Royal Society' ('Roy. Soc. Proc.' vol. 43, p. 140 (1890)). Observations on seventy-two persons confirmed Lord Rayleigh's results. There was, however, one woman who had the peculiarity of requiring an exceptional amount of green in matching the yellow. Her husband was normal, but, among three sons, two were affected in the same way as herself.

When Lord Rayleigh resigned the Cavendish Professorship at the end of 1884, the laboratory had established its reputation as a research institution, and he left behind him a number of devoted workers. At the same time, he had gained experience which could not fail to have had a marked influence on his future work. When he came to Cambridge, although he must have been conscious of his great aptitude for designing and carrying out experiments, he began the conduct of delicate and accurate measuring operations with great diffidence. This diffidence, a result of the cautious tendency of his mind, proved to be a valuable factor of safety, preserving him from the danger of over-confidence and keeping him on the constant look-out for unsuspected errors. He never felt satisfied until he had confirmed his results by different methods, and had mastered the subject from all possible points of view. The group of researches, in which he aimed at numerical accuracy, culminated in the discovery of Argon, but ten years intervened between his departure from Cambridge and the ultimate achievement. In the meantime, a number of other investigations demand attention.

Important contributions were made by Rayleigh to certain problems connected with the propagation of waves, more especially in cases where the wave-velocity depends on the period. The most familiar instance is that of deep sea water waves. When a group of such waves advances, we can either fix our attention on a particular wave or on a group as a whole, and we shall find that the group advances with only half the velocity of the wave. The wave passes through the group, and dies out at its front, while fresh waves arise at the tail end. The subject had already been considered by Stokes and Osborne Reynolds, but Lord Rayleigh in his book on Sound, published in 1877, gave a simple formula which allows us to calculate in all cases the group velocity if the relation of the wave-velocities to the wave-length be known. In the particular instance of flexural waves in rods or bars the group moves with twice the velocity of the wave, thus reversing the case of deep water waves. What holds for waves on water or in elastic solids must also hold for light waves, and when we measure the velocity of light by means of the eclipses of Jupiter's satellites, or by Fizeau's toothed wheel, we really determine the group velocity, which, in a dispersive medium, is not identical

with the wave-velocity. It is not quite so obvious that this is equally true when Foucault's method of the revolving mirror is used, but as Willard Gibbs pointed out, the general proposition is maintained also in this case. A more difficult question arises in connection with the aberration of light. In a paper published in 1881, Rayleigh assumed that this depends on the wave-velocity, and therefore provides a practical means of discriminating between wave-velocities and group-velocities in interstellar space, but on reconsideration (vol. 6, p. 41) he acknowledges the justice of Ehrenfest's criticisms, and confirms that the rate of propagation of groups of waves is in this case also the determining factor.

Another application of the theory of wave-propagation was made in 1885. Rayleigh pointed out that waves passing along the surface of an elastic body probably play an important part in earthquakes, inasmuch as, spreading only in two dimensions, their intensity will gain the upper hand at great distances compared with waves spreading through the interior of the earth. This surmise was subsequently fully confirmed, and the Rayleigh waves are now recognised as an important feature in seismograms. Thus in the records of the great Messina earthquake, Prince Galitzin could trace at Petrograd the surface waves which had travelled round in the earth in opposite directions and from his seismograms deduced their velocity of propagation as being 3.53 kilom. per second. There is a good agreement between this value and that calculated from Rayleigh's formulæ, when plausible assumptions are made with regard to the elastic properties of the materials contained in the upper part of the earth's crust.

Another short paper may here be mentioned, which leads to a result surprising at first sight, but incontrovertible and almost obvious when the conditions of the problem are clearly recognised (vol. 2, p. 417). In what way does the illumination inside a thick cloud or in a fog vary with the distance from the illuminating source or with the direction? The answer is that "at any distance from the source, and whatever the distribution of clouds, there is always in every direction the full radiation due to the temperature of the source, provided only that there be outside a complete shell of cloud sufficiently thick to be impervious."

There is perhaps no better example of the ample harvest so frequently brought to fruition by Rayleigh's generality of vision, concentrating in one focus apparently diverse trains of reasoning, than that furnished in a paper (vol. 3, p. 1), published in 1887. It begins by referring to a previous investigation concerning Melde's experiment in which a string is maintained in transverse vibrations by connecting one of its extremities with the vibrating prong of a tuning-fork. Our mind is then switched off to the Lunar Theory. In Rayleigh's own words: "My attention was recalled to the subject by Mr. Glaisher's address to the Astronomical Society, in which he gives an interesting account of the treatment of a mathematically similar question in the Lunar Theory by Mr. Hill and by Prof. Adams." A few pages are devoted to a differential equation which occurs in the Lunar

Theory, and it is pointed out that a certain constant which, in the astronomical problem, must be real, leads to acoustical applications when it becomes imaginary. The vibrations propagated along a stretched string periodically loaded at equal intervals are discussed, as a simple example illustrating the mathematical results, and the conditions are determined under which the vibrations propagated in one direction ultimately suffer total reflexion. But the acoustical problem is only a step leading to Optics. Periodic structures here are used to explain the brilliant reflected tints such as are seen on superficially decomposed glass. Having started with Acoustics, passed on to the Lunar Theory, and finally to Light, a far-seeing prophecy is relegated to a footnote which must be quoted in full:

“A detailed experimental examination of various cases in which a laminated structure leads to a powerful but highly selected reflexion would be of value. The most frequent examples are met with in the organic world. It has occurred to me that Becquerel’s reproduction of the spectrum in natural colours upon silver plates may perhaps be explicable in this manner. The various parts of the film of subchloride of silver with which the metal is coated may be conceived to be subjected, during exposure, to *stationary* luminous waves of nearly definite wave-length, the effect of which might be to impress upon the substance a periodic structure recurring at intervals equal to *half* the wave-length of the light; just as a sensitive flame exposed to stationary sonorous waves is influenced at the loops but not at the nodes (‘Phil. Mag.’ March, 1879, p. 153; vol. 1, p. 406.) In this way the operation of any kind of light would be to produce just such a modification of the film as would cause it to reflect copiously that particular kind of light. I abstain at present from developing this suggestion, in the hope of soon finding an opportunity of making myself experimentally acquainted with the subject.” To this is added in 1900: “I need hardly remind the reader of the beautiful coloured photographs which M. Lippmann has since obtained by this method.”

Rayleigh accepted the Secretaryship of the Royal Society on the resignation of Sir George Stokes in November, 1885, and held the office during eleven years. Additional duties thus fell upon him, in connexion with which it is appropriate to quote the remarks he made in the Obituary Notice of his predecessor: “And the reader of the Collected Papers [of Stokes] can hardly fail to notice a marked falling-off in the speed of production after this time [the appointment to the Secretaryship]. The reflexion suggests itself that scientific men should be left to scientific work and should not be tempted to assume heavy administrative duties, at any rate until such time as they have delivered their more important messages to the world.” Lord Rayleigh no doubt felt the additional responsibilities of his office, but there was no reduction of output. In his case the number of papers published may serve as a rough measure of scientific production, because he never published without having something substantial to communicate. The following table, in which that number is given for successive

intervals of five years, is therefore of some interest. It will be seen that with the exception of the remarkable period during which he worked at the Cavendish Laboratory, and published at the rate of twelve papers a year, most of them being of considerable importance, his productivity was surprisingly constant:—

	Number of papers published.
Before 1871	5
1871-1875	32
1876-1880	33
1881-1885	60
1886-1890	46
1891-1895	41
1896-1900	45
1901-1905	48
1906-1910	39
1911-1915	52
1916-1919	45

The Senior Secretary of the Royal Society, Sir Michael Foster, no doubt attended to much of the routine work, but it is needless to say that Rayleigh never grudged the time and thought spent on the adjudication of papers presented to the Society for publication.

Perhaps the most important result of his Secretaryship was his rescue of Waterston's important paper that had been relegated to the archives of the Royal Society in 1846. In an introduction to its publication in the 'Philosophical Transactions,' forty-six years after it was read before the Society, Rayleigh explained the circumstances which led him to search for the paper, and expressed the opinion that "the omission to publish it at the time was a misfortune which probably retarded the development of the subject by ten years." A marked service to the history of science was thus rendered by rescuing from oblivion the memory of a somewhat mysterious personality who, after spending a good part of his life as a naval instructor in India, disappeared, one year before Rayleigh took over the Secretaryship, having left his lodgings in Edinburgh for an evening walk, never to be seen again.

It was during the second year of Rayleigh's tenure of office that the 'Transactions' were divided into separate volumes, marked "A" and "B," containing respectively the physical and biological papers. The corresponding change in the 'Proceedings' was made in 1905.

The important experimental investigations on the density of gases which Rayleigh was carrying out during this period might have satisfied anyone less fertile in new ideas or rapid in devising means of submitting them to a crucial test, but many other problems were attacked simultaneously. His researches on capillary forces, both theoretical and experimental,

advanced the subject in many directions, and led to several results of fundamental importance. It has already been described how the study of the instability of jets brought the subject of surface tension to his notice. He continued his investigations in 1882 and 1883, and resumed them again after a further interval of seven years.

The theory of capillary forces indicates that surface tension is a physical constant depending only on the properties of the two bodies in contact. If a plane film of soap solution, such as may easily be produced inside a wire frame, be held horizontally, equilibrium requires, in accordance with the theory, that the tension is the same at every point of the film. Most of us probably have observed without surprise that the film maintains its continuity when placed vertically, though a little reflexion will show that this is irreconcilable with the assumption that, in this case at any rate, tension is independent of the thickness of the film. If the surface forces are the same in all parts of a vertical film, there is nothing to counterbalance gravity and the central portions of the film ought to fall down with the acceleration of a free body. To maintain equilibrium, the tension in the higher parts must be greater than that which is effective in the lower portion. The difficulty here is to bring the facts into harmony with the theory. The simplest explanation, according to Rayleigh, is to adopt a suggestion of Marangoni dating back to 1871, according to which the body of the film is covered by "a coating or pellicle composed of matter whose inherent capillary force is less than that of the mass." It was suggested by Marangoni that the coating was due to contamination from the outside. In a vertical film the pellicle would thicken in the lower portion and would therefore diminish the surface tension to a greater extent than in the upper portions. Rayleigh's first contribution to the subject was suggested by the consideration that if this were true the pellicle would take time to form, and that freshly established liquid surfaces might behave differently. There was already some confirmation of this in Marangoni's observation that within very wide limits the superficial tension of soap solutions, as determined by capillary tubes, is almost independent of strength. The difficulty was to devise some arrangement for measuring the capillary forces in surfaces directly after their formation. This problem was solved by Rayleigh, and the experimental arrangement supplied by his previous researches on liquid jets. When such a jet passes through an elongated aperture, the elongation in the original direction quickly disappears and the cross section becomes circular, to be replaced in its turn by an elongation at right angles, and so alternately backwards and forwards. The jet takes up a chain-like appearance, and the period of the alternate contractions and elongations supplies a means for evaluating the surface tension, which should vary as the inverse square of the wave-length. The experiments completely proved that freshly-formed surfaces of solutions of oleate of soda in water have a considerably higher surface tension than that deduced from the rise in capillary tubes. The latter was about one-third of that observed with water, and remained

constant while the proportion of the oleate was increased from 0.25 to 2.5 per cent. At the same time the surface tension as calculated from the jet increased in the ratio of 5 : 6, being nearly the same in the more diluted solutions as in water. The time required to form the pellicle is of the order of 0.01 seconds.

Once the existence of these pellicles was recognised it became important to examine their constitution and behaviour. The violent movements of bits of camphor scrapings when placed on clean water surfaces are well known. If the surface be greasy the movements are stopped. It was interesting to determine the thickness of a film of oil necessary for the purpose. The quantity of oil was measured by weighing a platinum wire first clean and then charged with a little olive oil. This oil was then spread over a circular surface of water, 33 inches in diameter, and it was found that a thickness of about two-millionths of a millimetre was sufficient to stop completely all movements of the camphor particles. This thickness is equal only to the 300th part of the wave-length of blue light. A further effect of the pellicles is observed in the so-called superficial viscosity of water. This had been investigated by Plateau, who allowed a magnetic needle to swing in contact with water, either when totally immersed or when only its lower surface was in contact with the liquid. In the latter case it came to rest much more quickly. The result of the experiment was that the thickness of the film of oil at which the surface viscosity began to be noticeable is only the sixteenth part of that which is effective in the camphor experiment. A small correction is necessary, because in the observations relating to surface tension special precautions were taken to clean the water surfaces, while tap-water was used in the camphor experiments. The total thickness of oil necessary to stop the movements should, therefore, be raised by the amount which was present before the oil was added, and this Rayleigh estimates to be about 20 per cent. of the thickness of oil that was added.

One of the methods devised by Rayleigh to clean the surface of a liquid depended on the action of an expansible hoop of thin sheet brass. When the hoop is placed in the basin of water so that it includes as little of the water as possible, and then expanded until its shape is circular, the inside surface of the water is freshly formed and should be almost perfectly clean. In a further set of experiments the surface tension of clean water was measured by observing the velocity of propagation of ripples formed by a needle dipping into the water and attached to a tuning-fork. The research presented many difficulties overcome with great ingenuity.

Further papers followed, in which the theory of surface forces is examined critically and historically, and the theory is extended so as to include compressible liquids.

The impossibility of keeping any surface exposed to air free from a film of greasy matter, leads us to expect an appreciable and perhaps important influence in other phenomena in which the surface plays a part. Such is, for instance, the reflexion of light. According to theory, there should be an angle of incidence at which the reflected ray is completely polarized, but

experiment shows that the component which ought to be absent never disappears entirely. An observation was made by Drude in 1889, indicating that the polarization at a freshly split surface of rock salt is very nearly complete, but deteriorates on standing, and this suggested that contamination of the surface was the dominating cause of the discrepancy between theory and experiment. Lord Rayleigh had examined nearly contemporaneously the reflexion from clean liquid surfaces. After a temporary failure, due to a defective optical appliance, Rayleigh returned to the subject in October, 1891, with the result that the polarization at the proper angle of incidence was found to be nearly perfect when the surfaces were thoroughly clean. There is, indeed, in the case of water and some other liquids, a small residual effect in a direction opposed to that observed with surfaces that have been exposed to air.

Returning to the subject in 1908, Rayleigh extended his observations to glass, and again found that, with freshly polished surfaces, the residual polarization in the plane of incidence was reversed. But some unexpected results were obtained with regard to the cause of deterioration. Moisture alone, or even grease, did not appear to have any marked effect, but the glass itself seemed to be attacked by some constituent of the air; the exclusion of carbonic acid retarded the process of deterioration. The paper (vol. 5, p. 489) concludes with the remark: "Surface phenomena generally offer a wide field for investigation, which might lead to results throwing much needed light on the constitution of matter." Experiments with diamond and fused quartz, described in 1912, gave similar results. If it be remembered that the thickness of the film which disturbs the balance upon which the absence of one component at the polarizing angle depends, is a small portion of the wave-length of light, the great delicacy of the optical test becomes apparent.

One further contribution to science, dealing with the increase in the efficiency of a steam engine, which may be expected from superheating or a raising of the boiling-point by chemical means, may be noticed at this stage (vol. 3, p. 538). It suffices to quote the last sentence of the paper in which the subject is discussed: "In conclusion, I will hazard the prediction that, if the heat-engines of the distant future are at all analogous to our present steam-engine, either the water (as the substance first heated) will be replaced by a fluid of less inherent volatility, or else the volatility of the water will be restrained by the addition to it of some body held in solution."

Sensational discoveries are often the result of opportunities well used, but presenting themselves accidentally. Such was the case, for instance, with radioactivity, the first indications of which were due to the accidental passage of a cloud across the sun's disc, which disposed of an erroneous theory, and put Henri Becquerel on the right track. In contrast with such surprises which unexpectedly convert the experimenter into a discoverer by the grace of accident, the new gas "Argon" entered into the family of elements independently of any favourable accident. Its discovery flowed

out of a well-designed series of experiments conducted with a definite purpose, and though the most important of the results arrived at was not anticipated, it came as a well-deserved reward for a strictly scientific procedure which concentrated all possible methods of attack upon one object, perfecting these methods until all discrepancies were cleared up.

It all arose out of the interest, dating back to his Cambridge period, that Rayleigh took in Prout's law, or—as it should be more correctly styled—Prout's hypothesis, according to which all atomic weights are integer numbers. As the exact determination of the relative combining weight of Oxygen and Hydrogen seemed to furnish the most promising test, Rayleigh proposed to determine as accurately as possible the relative densities of the two gases, and to combine the results arrived at with the volumetric analysis of the products of decomposition of water. The latter—as he knew—was being undertaken by Alexander Scott. In a preliminary note published in 1888, he gave, as the most probable result of a set of experiments, 15·884 for the ratio of the densities. A subsequent communication contained the description of experiments in which weighed quantities of hydrogen and oxygen were united by sparking, and the residue measured. This method gave 15·89 for the ratio of atomic weights. After the publication of Prof. Morley's extensive researches on the ratio of volumes, Rayleigh reverted to his original intention of concentrating efforts on the determination of densities, which, though the method was perfected, yielded a number (15·882) only slightly less than that contained in his first communication. Adopting Prof. Morley's results for the volumetric composition of water, the ratio of atomic weights would be 15·880, but, according to later determination by Alexander Scott (quoted by Rayleigh, vol. 4, p. 52), this figure should be reduced to 15·863.

He next turned his attention to nitrogen. We find the first published communication on the subject in a letter to 'Nature,' which appeared in the issue of September 29, 1892. "I am puzzled," he writes, "by some results on the density of nitrogen, and shall be obliged if any of your chemical readers can offer suggestions as to the cause. According to the methods of preparation I obtain two quite distinct values. The relative difference, amounting to about 1/1000 part, is small in itself, but it lies entirely outside the errors of experiment, and can only be attributed to a variation of the character of the gas."

In the first method, the oxygen of atmospheric air was removed in the ordinary way by metallic copper, while in the second method part of the nitrogen was supplied by the decomposition of ammonia. The ammonia made gas was the lighter of the two, and conceivable sources of error through contamination or otherwise failed to explain the discrepancy. The only suggestion in this communication is contained in the query: "Is it possible that the difference is independent of impurity, the nitrogen itself being to some extent in different (dissociated) state?" This letter failed to elicit any valuable suggestion.

If we proceed in chronological order we have next to notice the communication printed in the 'Proceedings' of the Royal Society during 1893, "On the Densities of the Principal Gases." Important improvements were made in the methods used by previous observers. In these the pressure of the gas to be weighed was adjusted by equalising it with that of the outer air, which itself was measured with the help of a barometer. In order to avoid the sources of error that may be introduced by this procedure, Rayleigh placed inside his apparatus a manometer, the principal part of which consisted of a measuring rod carrying steel points at its upper and lower extremities, the pressure being always adjusted so that these steel points were in optical contact with the upper and lower mercury surfaces of the manometer. Throughout the experiments the pressure was therefore rigorously constant. In the reductions, an error that had been overlooked by all previous experimenters was allowed for. When the gas is obtained by comparing the weights of a vessel before and after filling, it never seems to have occurred to these observers that the volume is different in the two cases, owing to the contraction of an evacuated vessel due to outside pressure. The consequent difference in buoyancy may introduce errors amounting to over two parts in 10,000. The figures obtained giving the densities under normal conditions of air for oxygen, nitrogen (including its Argon content), and hydrogen will probably remain for some time to come the most accurate determination of the densities of these gases. The anomaly that occurred with nitrogen prepared from different sources was briefly referred to in these words: "Although the subject is not yet ripe for discussion, I cannot omit to notice here that nitrogen prepared from ammonia, and expected to be pure, turned out to be decidedly lighter than the above. When the oxygen of air is burned by excess of ammonia, the deficiency is about 1/1000 part. When oxygen is substituted for air, so that all (instead of about one-seventh part) of the nitrogen is derived from ammonia, the deficiency of weight may amount to $\frac{1}{2}$ per cent. It seems certain that the abnormal lightness cannot be explained by contamination with hydrogen, or with ammonia, or with water, and everything suggests that the explanation is to be sought in a dissociated state of the nitrogen itself."

In April, 1894, the subject is again referred to in a communication to the Royal Society, in which experiments are described showing that when nitrogen is prepared by passing nitric oxide, nitrous oxide or ammonium nitrate over red-hot iron, the density has the same low value as when it is derived from ammonia. On the other hand, whether the oxygen of the air was removed from the air by hot iron or ferrous hydrate, the higher value held good. It was stated in conclusion that nitrogen prepared from oxygen and ammonia is about $\frac{1}{2}$ per cent. lighter than ordinary nitrogen, and stored in the globe for eight months was found not to have increased in density. This experiment, as Rayleigh subsequently explained in a lecture to the Royal Institution, was intended to test the possibility that the lighter nitrogen included a certain number of dissociated molecules containing only one atom. If this were the

case, it was to be expected that the nitrogen should gradually become denser by recombination.

The question now arose: "What was the evidence that all the so-called nitrogen of the atmosphere was of one quality." On consulting Sir James Dewar, Lord Rayleigh was referred to Henry Cavendish's experiments in which the nitrogen of the air was oxidised by sparking, and after the nitrous oxide had been absorbed by potash, it was found that a residue was left. The conclusion drawn by Cavendish was that if there was more than one inert gas in the atmosphere, the second ingredient could not amount to more than 1/120th part. The only inference that could legitimately be drawn from these experiments was the one adopted by Cavendish, who concluded that "phlogisticated air" (*i.e.*, air deprived of oxygen) was substantially of one kind so far as its power of combining with oxygen was concerned. Whether the small residue left over indicated the presence of another gas was hardly to be settled with the experimental facilities available at the time. But the method had further possibilities under modern conditions. As soon as Lord Rayleigh's attention had been called to these experiments, he set to work and found that, after elimination of the nitrogen, some non-oxidisable gas persisted to show itself in spite of all precautions. The experiments left no doubt that the atmosphere contained a new constituent, though the question as to whether this was a new element or a compound was still open. Excess of cautiousness kept Rayleigh from announcing the discovery, probably on account of the residue not being strictly proportional to the quantity of air used; this was subsequently shown to be due to the absorption of the new gas by water. At this stage Sir William Ramsay joined the research. In his own laboratory he confirmed Lord Rayleigh's work and isolated the new gas, absorbing the nitrogen of the air by means of red-hot magnesium. The discovery was first announced at the British Association meeting at Oxford, and the great paper on "Argon, a new Constituent of the Atmosphere" was communicated to the Royal Society jointly by Lord Rayleigh and Sir William Ramsay on January 31st, 1895. In this paper the various methods of removing the nitrogen from air are examined in detail. It was shown that the new gas, whether prepared by the method of Cavendish, or by magnesium had the same density, within the limits of error; the spectrum of Argon was described, and its solubility in water measured. By a most important series of experiments the ratio of the specific heats was determined, and was found to be 1.66, which proved the gas to be monatomic. It was through this last result that Lord Rayleigh became fully convinced that the new gas was an element. All attempts to discover some chemical reaction of the gas proved abortive: hence the name "Argon" (*Ἄργον*).

At various times Lord Rayleigh took occasion to emphasise with characteristic generosity that the paper in which the discovery of Argon was announced was the joint work of Sir William Ramsay and himself. Without wishing to qualify that declaration, it seems necessary to define clearly the stage at which collaboration began, more especially as some published state-

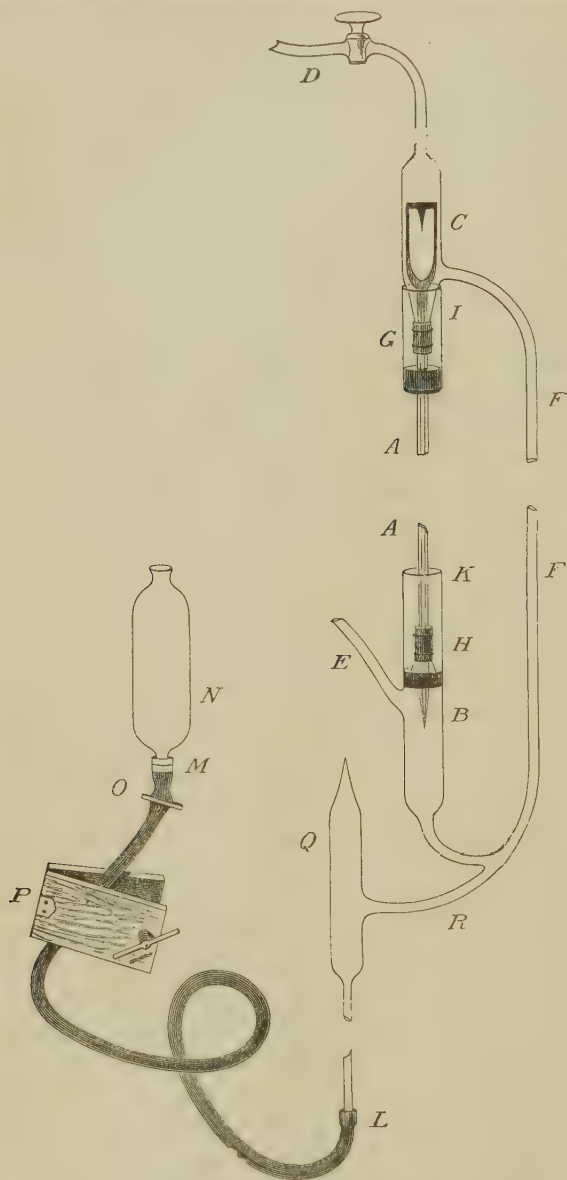
ments accessible to future historians may convey a wrong impression. Lord Rayleigh accepted the assistance of a trained chemist, not because he had come to the end of his own resources, but because the investigation could thus be

carried out more quickly, and in some respects more thoroughly, by including the chemical as well as the physical properties of the gas. Putting aside his own personality, he adopted the course which seemed to him to be most conducive to the progress of science. But the fact remains that he had, without help from others, isolated Argon. He accepted collaboration, but did not ask for it.

In a later communication Lord Rayleigh repeated the density determinations of Argon on a larger scale, and arrived at the figure 19.940 (Oxygen = 16). The refrangibilities of Argon and Helium were determined, as well as their viscosities.

Rayleigh's device of adjusting the pressure of a gas with the aid of a manometric gauge has already been mentioned. It was designed in order to minimise the inaccuracies incumbent on the usual methods of measuring the displacements of a column of

mercury. In these the length to be measured is separated from the scale with which it is to be compared by a thickness of glass which may not be uniform, and hence introduce complications and unavoidable errors. Lord Rayleigh's procedure introduces a novel feature, and marks



what may without exaggeration be called a revolution in the accurate determination of gas pressures. In view of the further extension of the same principle, which greatly increased the range of its possible applications, the gauge in its simplest form is illustrated in the accompanying figure, copied from the first paper on the densities of gases (vol. 4, p. 39). The greater part of the mercury to which the pressure is due is contained in the connecting tube FF. The temperature is taken by a thermometer whose bulb is situated near the middle of FF. B and C are two points which may be said to be the terminals of the steel rod AA. Their distance from each other may be measured accurately before insertion into the apparatus, and they can, by means of a plumb line, be made to lie in the same vertical line. If a vacuum be established in the upper part through D, and, as described in the paper, the points B and C brought simultaneously into optical contact with the two mercury surfaces, the pressure in a vessel connected with E is determined by a column of mercury of known length. No less ingenious than the original device are the modifications which allow the same principle to be applied to changes of volume with changes of pressure. The first of these is described in a paper (vol. 4, p. 511): "On a New Manometer and on the Law of Pressure of Gases between 1.5 and 0.01 millimetres of Mercury." The two mercury surfaces which determine the pressure are now placed side by side in the two branches of a U-tube, instead of vertically above each other. The pointers—made of glass—are adjusted so as to lie in the same horizontal plane. If the upper branches of the U-tube open out to the atmosphere, simultaneous contact shows that the adjustment is correct. Slight deviations are corrected by tilting the apparatus. If one branch of the U is connected to a vacuum and the other to a vessel containing a gas at low pressure, simultaneous contact can again be secured by tilting the apparatus. This was measured optically, and the distance between the points being known to 0.1 of a millimetre, varying pressures up to 1.5 mm. of mercury could be measured to $1/2000$ of a millimetre. In two further papers, published in 1902 and 1905 respectively, Lord Rayleigh bridged over the gap between these low pressures, at which Boyle's Law was thus established to a high degree of accuracy and atmospheric pressure. Returning to the original form of the manometric gauge, two of these as nearly similar as possible were used, the similarity, being tested by combining them "in parallel." If the similarity be complete, and they be then used "in series," we are enabled to obtain a pressure exactly double that obtained by employing the gauges separately. The results may be summarised in the following table which gives the value of p_1v_1/p_2v_2 , where $p_2 = 2p_1$, the pressures in millimetres of mercury having values indicated at the heads of the columns. Excess of the figures in the table above unity indicates a higher compressibility than that required to satisfy Boyle's Law :—

Pressures.	380-760.	75-150.
Oxygen	1·00038	1·00024
Hydrogen	0·99974	0·99997
Nitrogen	1·00015	—
Argon	—	1·00021
Air	1·00023	0·99997
Carbonic oxide.....	1·00026	1·00005
Carbonic dioxide.....	1·00279	—
Nitrous oxide	1·00327	1·00066

Lord Rayleigh's earlier work on the theory of optical instruments dealt primarily with telescopes and spectroscopes. In 1896 he extended his investigations to the microscope. The distinctive peculiarity of this instrument consists in the circumstance that the light illuminating the various parts of the object is derived from the same source. Adjacent points of the object cannot therefore be treated as if they were self-luminous, and, if the images of such points partially overlap, there is a phase relation in the overlapping portions which has to be taken into account. Abbé was the first to overcome the difficulty by a novel method of treatment which marked a great advance, and "contributed powerfully to the modern development of the microscope." But the success of this method in bringing out the distinctive properties of the microscope in certain simple cases led to an exaggerated view of its generality. It is, in reality, more limited in its range of application than the older method, which, as Rayleigh showed, is quite capable of dealing with the whole problem. Rayleigh co-ordinated the two methods and discussed their relative merits. The essence of the matter is contained in two significant passages, to be found in the first of the two papers relating to the subject: "In the case of the telescope, we have to do with a linear measure of aperture and an angular limit of resolution, whereas, in the case of the microscope, the limit of resolution is linear, and it is expressed in terms of angular aperture." "It seems fair to conclude that the function of the condenser in microscopic practice is to cause the object to behave, at any rate in some degree, as if it were self-luminous, and thus to obviate the sharply-marked interference bands which arise when permanent and definite phase relations are permitted to exist between the radiations which issue from various points in the object." The second of these quotations is one of the most illuminating remarks that has yet been made on the Optics of the Microscope.

There is no more alluring source of error in physical science than that which springs from an elusive sense of security induced by a mathematical investigation, which is perfectly correct, but rests on certain simplifying assumptions that happen to be unfulfilled in the problem to which it is applied. The great majority of the problems of diffraction which are of interest to the physicist can be explained by elementary reasoning, and he is tempted to apply this same reasoning regardless of the conditions which

limit its application. He is then liable to fall into serious error, from which only a careful study of Lord Rayleigh's investigations can preserve him. Thus in a paper published in 1907 "On the Dynamical Theory of Gratings," Rayleigh describes a reflecting grating in which alternate parts are equally wide but so disposed as to form grooves of depth equal to a quarter wave-length. According to the elementary theory, it seems almost obvious that if light fall on such a grating perpendicularly, the central image is obliterated, the whole light being concentrated in the lateral spectra. This is approximately true if the grating interval be wide enough, but it is otherwise when this interval is reduced to less than the wave-length. As Rayleigh remarks: "The conclusion is now entirely wide of the mark. Under the circumstances supposed there are no lateral spectra, and the whole of the incident energy is necessarily thrown into regular reflection, which is accordingly total instead of evanescent. A closer consideration shows that the recesses in this case act as resonators in a manner not covered by Fresnel's investigations, and illustrates the need of a theory more strictly dynamical." The paper supplies that need to a great extent, and incidentally shows how very complicated the complete solution of the problem becomes. The most serious of the complications arise already with a single aperture, and three papers are devoted by Rayleigh to the subject. The first of these deals generally with plane waves of a simple type, which may be waves of condensation and rarefaction, as in sound or electric waves. "Ultimately one or both dimensions of the aperture will be regarded as infinitely small in comparison with the wave-length, and the method of investigation consists in adapting to the present purpose known solutions regarding the flow of incompressible liquids." In two papers dealing more particularly with the light transmitted through narrow slits in infinitely thin perfectly opaque screens (vol. 5, p. 410; vol. 6, p. 161), an experimental result observed by Fizeau is examined and explained. "It appears that if the incident light be unpolarized, vibrations perpendicular to the slit preponderate in the transmitted light when the width of the slit is very small, and the more the smaller this width." With somewhat wider slits, such as scratches upon silvered glass, the opposite polarization prevails. "If the width of the slit were about one-third of the wave-length of yellow-green, there would be distinctly marked opposite polarizations at the ends of the spectrum." But, as the author points out, the conclusion does not hold for ordinary spectroscopic slits, it being one of the conditions of the calculation that the screen containing the aperture should be infinitely thin. In connexion with the same subject we find an interesting Note (vol. 5, p. 405), which supplies the explanation of an observation by Prof. O. W. Wood on a remarkable anomaly in the distribution of brightness in different spectra. At a certain angle of incidence a certain grating was found to show one of the D lines of sodium and not the other. It appears from Rayleigh's discussion of the problem, that the anomaly is connected with the disappearance of a spectrum of higher order. Thus in the spectrum of the first order "an abnormality might be expected at a

particular wave-length, if, in the third order, light of this wave-length were just passing out of the field of view, *i.e.*, were emerging tangentially to the surface."

The science of Optics is rich in the record of observations, which, as already pointed out, fail to be fully explained by the approximate formulæ in common use. We are apt to disregard minor discrepancies, because we feel convinced that more accurate calculations, or a greater perfection of the experimental conditions, would bring the accepted theories into complete accord with the facts. But such partially unexplained phenomena had a peculiar attraction for Rayleigh. Without anticipating any revolutionary new results, he did not feel happy so long as he was without a clear insight into the source of the difficulty, and it often happened that the solution, when once found, had important bearings on related phenomena. As an instance, an observation by Stokes of some peculiar internal coloured reflection in crystals of chlorate of potash may be quoted. It seemed to Rayleigh that a reflexion from a single surface could not account for the bright colours that were observed, but that the structure must be laminated, so as to provide multiple reflexions. This conclusion was not, perhaps, difficult to arrive at, but it led Rayleigh to examine more closely the propagation of light through media possessing a periodic structure. A paper bearing on this question, in which Lippmann's method of colour photography is anticipated, has already been mentioned. Further extensive mathematical investigations of the problem were published by the Royal Society in 1912 and 1917. But all through these investigations Rayleigh was mindful of their bearing on a question in which he was highly interested: the explanation of the vivid colours shown in animal structures such as beetles' wings. In one of the last papers published before his death, he discusses the various theories which have been proposed to account for these colours, maintaining—though with some reserve—his own predilection for the one which depends on interference in the beam reflected from a laminated medium, or one possessing a periodic structure.

While the historical sequence of the problems which attracted Rayleigh's attention has hitherto—so far as possible—been followed, many important investigations were omitted in order to preserve a certain continuity in the subjects that have been discussed. To these we must now return, without pretending to cover the entire ground.

One of the many difficulties of the dynamical theory of gases is the breakdown of the general theorem of equipartition of energy in the case of its distribution among the different periods of radiation emitted by a hot body, and it ultimately required the introduction of an entirely new conception to remove this stumbling block. Without departing from the strictly mechanical ideas which were then universally accepted, Rayleigh examined the nature of the motion which gives rise to white light. The common view of considering such light as being made up of a collection of homogeneous radiations of adjacent periods involves a discontinuity, a continuous spectrum being

regarded as a spectrum of lines which are so close together that our instruments cannot separate them. Though such a view is justifiable in practice, it carries us no further if we wish to obtain an insight into the nature of the molecular movement which originates the continuous spectrum. The alternative is to look on white light—in the manner of Gouy—as being made up of a succession of irregular impulses. In order to account for the distribution of energy between the different frequencies, the impulses cannot be arbitrary: they must possess a finite duration and have a definite structure. An attempt to define that structure is made by Rayleigh (vol. 3, p. 268), with the result that the simplest case which can be treated mathematically leads to a law of radiation which, though it had actually been proposed by H. F. Weber, is not in accordance with observed facts. Eleven years later (1900) Rayleigh showed by simple reasoning that, assuming the law of equipartition to hold, the energy of radiation, within a specified small range of wave-lengths, should be proportional to the absolute temperature, and inversely to the fourth power of the wave-length; and the question is raised whether this may not be the proper form of the law for great wave-lengths. This important suggestion proved to be correct, as was fully established experimentally by Rubens and Kurlbaum. The new idea mentioned above, which accounts for the failure of the law of equipartition in the case of shorter waves, was introduced by Planck, who made the supposition that the energy of radiation is not infinitely divisible, but expressible in terms of a unit or “quantum” which is proportional to the frequency. The unit tending towards zero as the frequency diminishes, the agreement of the intensity distribution for long waves with the theory of equipartition is accounted for.

It is impossible to refer to all the acoustical problems discussed by Rayleigh but some mention should be made of his experiments on the perception of the direction of sound, which were continued at intervals during the whole period of his activity. The problem has a physiological as well as a physical aspect, and Rayleigh pushed its solution to a point at which it must be taken up by the physiologist, or possibly even the experimental psychologist. In 1875 he discovered that an observer could easily recognise whether a sound came from the left or from the right, but with pure notes it seemed impossible to distinguish between front and back. This inability, as was pointed out in a further communication, involves other ambiguities, because if the localisation of sound depends on the ratio of intensities as estimated by the two ears, it follows that for every direction towards the right front there must be a corresponding one towards the right back which is indistinguishable from it. Observations made with the assistance of Sir Francis Galton, who, being deaf in one ear, possessed hardly any power of locating sounds, supported the view that both ears are involved in the process of perception. Two explanations of our sense of sound direction have been offered. The first depends on the sound shadow thrown by the head, which would diminish the intensity of vibration at the ear farthest

from the source. The second explanation assumes some power of distinguishing differences in the phase of the sounds reaching the two ears. The relative merits of the two views were fully discussed by Rayleigh in a paper (vol. 5, p. 347) which formed the subject of the Sidgwick Lecture delivered at Cambridge in 1906. The first explanation, which seems the simplest, satisfactorily accounts for observations with high notes, but when the pitch of the note is such that the frequency is less than 128, the wave-length is several times greater than the diameter of the head, and the difference of intensities at the two ears becomes insensible. For low notes we must therefore fall back on the second explanation, and Rayleigh showed by a series of interesting experiments that a phase difference does indeed induce in our minds a sense of direction, which can be artificially produced if two notes of slightly different pitch are separately led one to each ear. The phase is then alternately ahead on one side and the other, and there is an apparent simultaneous change in the direction from which the sound appears to come. Students of the physiological aspects of acoustics will find much interesting information in Rayleigh's discussion of the manner in which the phase difference may be supposed to act, as also in the two papers in which he describes the results of his experiments on the nature and pitch of sibilants.

In the year 1909 Mr. Asquith, as Prime Minister, appointed an Advisory Committee on Aeronautics to direct the scientific work of a special department to be established at the National Physical Laboratory, and for general advice on the scientific problems arising in connection with the work of the Admiralty and War Office in aerial construction and navigation. Lord Rayleigh was nominated President of the Committee. His interest in the problems of flying dates back to an early period. As far back as 1883 he pointed out in 'Nature' (vol. 2, p. 194) that a bird cannot, either in still air or in a uniform horizontal wind, maintain its level without working its wings, and that hence the soaring of birds is impossible unless (1) the course is not horizontal, (2) the wind is not horizontal, or (3) the wind is not uniform. "It is probable that the truth is usually represented by (1) or (2), but the question I wish to raise is whether the cause suggested by (3) may not sometimes come into operation." When large birds are observed to maintain their average level in circular sweeps without any motion of their wings, they should rise against the wind and fall with it, if the effective condition of soaring depends on changes of wind velocity with altitude. This was one of the many predictions of Rayleigh that came true, as was shown by an independent observation of Mr. A. C. Baines on the sailing flight of the albatross. A full discussion of the problem will be found in the Wilde Lecture delivered at Manchester in 1900 (vol. 4, p. 462). The reports of the Aeronautical Committee contain several important contributions by Lord Rayleigh. The first of these draws attention to the important conclusions that can be deduced from the principle of "dynamical similarity." By means of it we may interpret the results

obtained with models of dimensions that are manageable in a laboratory, and apply them to cases where the magnitudes of the determining quantities are altered in suitable proportions. The principle of similarity has proved to be of the greatest importance in aerodynamics, and furnishes a scientific method of testing the construction of flying machines.

I am indebted to Prof. Horace Lamb for the following brief appreciation of Rayleigh's work on Hydrodynamics, from which a few passages referring to matters already mentioned have been omitted.

"Rayleigh's work on Sound and the theory of vibrations led by a natural transition to the study of water waves, where the same general principles are involved. His first paper (1876) on the subject deals with the conditions for wave-propagation without change of type, the problem being reduced to one of steady motion. The fundamental results of Airy, Stokes and others are thus obtained by a greatly simplified analysis. The theory of the 'solitary wave,' which had been studied experimentally by Scott Russell, is next investigated, and it is explained in particular why such a wave must necessarily be one of elevation only. In this work he had been anticipated by Boussinesq, who shares the credit of elucidating a matter which had long been a perplexity to mathematicians. The theory of deep-water waves of permanent type, which had been the subject of one of Stokes' classical researches, was also touched upon by Rayleigh in the above paper. It was to have a lasting fascination for him, and he returned to it at intervals almost to the end of his life, continually extending its approximations.

"The cognate theory of the ripples and waves produced when a local disturbance travels over a horizontal sheet of water at a speed exceeding a certain minimum had been outlined by Kelvin in the year 1871. The subject was in turn taken up and completed by Rayleigh, so far as the two-dimensional form of the problem was concerned. He also discussed the form of the ripples produced by a travelling point-disturbance. An analytical artifice which is introduced in this paper, and which subsequent writers have found very useful, may be referred to as characteristic. A mathematical indeterminateness, which presents itself in various problems of steady motion (owing to the implicit inclusion of free waves) when dissipation is neglected, is evaded by the temporary insertion of frictional terms varying as the velocity, whose coefficient is ultimately made to vanish. The indeterminateness is thus avoided, without the necessity of employing the true law of viscosity, with the elaborate analysis which this would involve.

"The theory of discontinuous motions in frictionless liquids had been originated by Helmholtz and Kirchoff in 1868 and 1869 in two classical papers. The work of the latter suggested to Rayleigh a theory of the resistance encountered by a plane lamina moving through a stream at a constant inclination, and he completed Kirchoff's solution from this point of view. The results, though not in complete accordance with more recent measurements, were a great improvement on previous explanations, and have stimulated much subsequent investigation. They may still claim, moreover,

to furnish the best *general* representation of the phenomena which we are as yet able to get by *a priori* dynamical reasoning. The friction over the surface of the lamina, and the formation of eddies in the wake, introduce qualifications which are as yet beyond the reach of calculation.

It had been remarked by Helmholtz, and further insisted upon by Kelvin, that a surface of absolute discontinuity in a frictionless liquid would necessarily be unstable. The question of stability of flow was of continual interest to Rayleigh, originally no doubt from its bearing on various acoustical phenomena, and later for its own sake. His first enquiry was: to what degree is the instability affected if the discontinuity is eased off, as it is in reality by viscosity? He found that the instability remains for disturbances whose wave-length exceeds a certain limit. He further investigated the case of flow between parallel planes, as the two-dimensional analogue of flow in a pipe, having in view Reynolds' experimental demonstration of a critical velocity. The motion proved to be stable provided the graph of the undisturbed velocity, as a function of distance from the medial plane, is free from inflexions. A similar conclusion was reached later for the case of a pipe. It is to be remembered that in these investigations the disturbance of the steady flow is assumed to be infinitesimal. Moreover, although the steady flow may be of the type which could be maintained under the influence of viscosity, the effect of friction on the disturbed motion is in fact neglected. In particular, the condition of no slipping at the walls, which appears to be fundamental, is violated. Calculations of the above type were resumed at frequent intervals, and his more recent papers include a masterly review of the subject, in which viscosity is duly considered. The theoretical problems which were set by Reynolds' experimental work must be regarded as still unresolved, but Rayleigh's papers have done much to clear the ground, and contain besides many points of independent interest."

Rayleigh's remarkable influence on contemporary science is due, in great part, to the example he set by his method of attack and exposition. His mathematical analysis never lost touch with realities, so that the lucid presentation of the nature of the problem, and the simple but precise reasoning along which the argument proceeds, allows even the non-mathematical reader to appreciate the bearing of the results, and the limitations to which the problem is subject. Maxwell once said that everyone is a mathematician, with the difference that some know it and others don't. Rayleigh seemed to have the power of bridging the gulf, and of presenting mathematical arguments in a form that can be appreciated, even if not followed in detail, by the tyro. This uncommon faculty is specially noticeable in his discussion of the law of Partition of Energy (vol. 4, p. 432), one of the most difficult subjects in mathematical physics, yet discussed with such exquisite simplicity and perspicuity that, whether mathematician or experimentalist, we must all feel whenever we return to it, that we have gained some fresh insight into the intricacies of this many-sided problem. Out of numerous similar examples that might be given, it must suffice to refer only

to one of his later papers, in which those interested in Fourier's theorem (vol. 6, p. 227) from the physicist's point of view cannot fail to find much instructive reading.

In his Presidential Address to the British Association, Lord Rayleigh, speaking of future progress in general chemistry, remarked: "And if I might without presumption venture a word of recommendation it would be in favour of a more minute study of the simpler chemical phenomena." It was not only in chemistry that the simple phenomena attracted him. Thus he examined the process of polishing and grinding glass, showing that the latter process acts by breaking out small fragments (pitting) while, as regards polishing, he concludes that (vol. 4, p. 546): "in all probability the process is a molecular one, and that no coherent fragments containing a large number of molecules are broken out. If this be so, there would be much less difference than Herschel thought between the surfaces of a polished solid and of a liquid." Simplicity was his great aim, not only in choosing the problem, but also in the procedure adopted to solve it. What could be more simple or more effective than the method designed by him for testing the accuracy of reflecting surfaces by immersing them in water? If the surface to be tested is levelled as nearly as possible and just covered by the water, the interference bands produced by the liquid film that stands above the reflecting surface indicate at once whether it is truly plane or possesses any local irregularities. In some cases the simplicity belongs to the problem rather than to the solution, as in the case of the familiar phenomenon of the scintillation of stars (vol. 4, p. 60).

When a subject which at first sight seems capable of easy experimental investigation presents formidable difficulties in the execution, Rayleigh showed his mastery in the design of experimental detail. Take, as an instance, the formula deduced by Fresnel for the intensity of light reflected by a polished surface. When the light is incident normally, the refractive index being μ , the amplitude of the reflected light in terms of that of the incident light should be $(\mu-1)/(\mu+1)$. There is no reason to suspect that the law is not accurate, but it was not in Rayleigh's nature to accept without verification a result, even when obtained by mathematical reasoning that appears to be irreproachable. I know of no problem in the whole range of Physics in which the planning-out of a satisfactory experimental arrangement was beset with so many difficulties overcome in so perfect a manner. The result disclosed a remarkable effect due to exposure to air, which may diminish the reflecting power of glass by as much as from 10 to 30 per cent. without any appreciable tarnishing being visible. A still more surprising fact was observed with a layer of silver deposited on glass, which gave a reflecting power more than 10 per cent. greater on the side exposed to air than on that in contact with the glass.

The limits to which an experimental investigation can be pushed was another of Rayleigh's favourite subjects. He showed how 4 c.mm. of a gas can be made to suffice in order to determine its refractive index; he

investigated the minimum current that could be detected by the telephone, the minimum condensation of air that affected the ear, and the sensibility of the eye to variations in wave-length.

Rayleigh's knowledge of the literature of science was extensive and thorough. In his own papers he invariably acknowledges, sometimes with almost excessive generosity, the work of others. His familiarity with the writings of John Herschel, Young, Lloyd, and authors that are little read, is illustrated in an excellent paper on the "History of the Doctrine of Radiant Energy" (vol. 3, p. 238). It was left to him to point out that Maxwell was the first to establish the equation which embodies the law of anomalous dispersion and is generally ascribed to Sellmeyer. Frequent references to historical matter appear in other papers.

Rayleigh's readiness to supply the explanation of puzzling observations may be illustrated by a short paper on "Coloured Photometry." The established fact here is that the eye has some power of comparing the intensities of luminous impressions due to light of different colours, and some physiological process is required to supply the common standard which makes the comparison possible. The power in question has an important application in the so-called "Flicker Photometer," and Rayleigh's suggestion is that the nerve irritation which causes the contraction of the iris by bright light furnishes the required measure. Two lights would then be physiologically of the same intensity when the tendency to contraction of the iris is the same for both.

Even at times when Rayleigh was most busily engaged in the researches which formed the main object of his activity, he did not lose interest in questions of fundamental importance raised by others. We find him discussing the problem: "Does chemical transformation influence weight?" and showing that an affirmative answer would point to some hitherto unsuspected thermal effects connected with gravitation.

Prof. Michelson's well-known optical investigations suggested the question whether the velocity of light in an electrolytic liquid is influenced by an electric current in the direction of propagation. Experiment gave a negative answer, and similar negative results were obtained on trying to find a possible effect of motion through the æther in causing double refraction, or an influence of the earth's motion on rotatory polarisation.

A man of Rayleigh's power and judgment could not help being frequently called upon to join deliberative bodies in which these qualities are required, and we all know that such external duties are formidable enemies to the conduct of research. Though reluctant to be drawn away from his scientific work, he never withheld his time and energy whenever he believed that he could give substantial assistance. The interests of Science were always placed above his personal inclination; and, especially in earlier years, he did not hesitate to decline a position, however honourable and influential, if he thought he could render better service to Science in his laboratory. In refusing the Presidency of the Royal Society in 1905, he

gave as his reason that he would be as good a President ten years later, while he did not then expect to be equally productive as a man of science.

He was one of the leaders of the movement which led to the establishment of the National Physical Laboratory, and acted as Chairman of the Committee of H.M. Treasury to report upon the desirability of its foundation. On the successful completion of the organisation he accepted the appointment of Vice-Chairman of the Board (the President of the Royal Society being "ex-officio" Chairman), and presided over the Executive Committee until shortly before his death. The services he rendered to the laboratory were invaluable, and greatly assisted the Director, Sir Richard Glazebrook, in raising it to its present unique position among the prominent scientific institutions of the world.

The contributions which Rayleigh rendered to Aviation as President of the Aeronautical Committee have already been mentioned. He was appointed to the Professorship of Natural Philosophy at the Royal Institution in succession to Tyndall in 1887, and held it during nine years. Though not by nature a ready speaker, his lectures were effective, and, like his writings, illustrate the truth of Buffon's saying: "*Ce qui se comprend bien s'énonce clairement.*" He fortunately included Abstracts of his Discourses at the Royal Institution in the 'Scientific Papers': they constitute a rich mine of beautiful experimental illustrations, covering important principles in almost all branches of Physics.

In 1896 he accepted the position of Scientific Adviser to Trinity House. This is an Association of English mariners which received its first charter from Henry VIII as a "Guild or Fraternity of the most glorious and undividable Trinity and of St. Clement." The guild received from Queen Elizabeth authority to erect beacons and other marks for the guidance of navigators along the coasts of England. It was subsequently divided between "Elder Brethren" and "Younger Brethren," the right of sole management being conferred on the former class. After various changes, the practical duties of the Brethren were confined to the erection and maintenance of lighthouses, buoys and beacons, and the supervising of pilots, while the Elder Brethren act as nautical assessors in the High Court of the Admiralty. In the 'Scientific Papers,' we find at least two problems on Sound suggested by Rayleigh's connexion with Trinity House; they both refer to fog signals. The first (vol. 5, p. 133) deals with the necessity of spreading the range within which the sound is heard as much as possible laterally while restricting it in the vertical plane. This requires the opening of the trumpet to be small in the horizontal and large in the vertical direction. That the theoretical conclusion is correct was verified with a trumpet emitting a high note, but it was pointed out that to carry out the idea on a large scale would mean a very large structure, the vertical dimension required for waves 48 inches long being of the order of 6 metres. A memorandum published in 1917 draws attention to the advantage of substituting wireless signals for fog horns on the ground

that these would supply information as to the direction of the origin of the signal.

In 1901 Rayleigh became Chief Gas Examiner, a position which carried with it the duty of arbitrating on disputed points.

A few words should be said with regard to Rayleigh's attitude towards some of the revolutionary notions which were beginning to shake the old foundations of Science. Like Stokes and Kelvin, he was brought up in the faith of Newton's doctrines, but the minds of the three men responded very differently to the first awakening of doubt. Kelvin felt strongly and expressed himself forcibly. To him the mechanism of the æther and of the ultimate constituents of matter could not be otherwise than the mechanism of the gross matter he could handle in the laboratory. That was the Alpha and Omega of his convictions. Stokes was more cautious; where Kelvin was angry, he only smiled mysteriously. In purely scientific matters, and in private conversation or unreported speeches, one suspected that Stokes had something of the iconoclast in his composition, and he enjoyed being told of any experiment that could not be reconciled to current theories. Rayleigh was purely judicial, repressing his personal predilections. To put it into colloquial language, where Kelvin would say: "This is all nonsense," and Stokes answer: "Perhaps; but all the same it is a hard nut for you to crack," Rayleigh would ask: "What is the evidence?" He did not hide his dislike of some of the modern theories, but he went far enough to admit that, if it be impossible to demonstrate experimentally the relative motion of a body and the æther, our belief in the existence of the æther must be reconsidered.

His attitude towards psychical research was mainly determined by his desire that there should be no limitation set to inquiry whatever the subject might be; and that personal prejudice should be excluded from every investigation. The last occasion on which Lord Rayleigh addressed an audience was in April, 1919, when he delivered his Presidential Address to the Society of Psychical Research, his final judgment being summed up in one of the concluding passages of that Address: "I fear that my attitude, or want of attitude, will be disappointing to some members of the Society who have outstripped me on the road to conviction, but this I cannot help. Scientific men should not rush to conclusions, but keep their minds open for such time as may be necessary. And what was at first a policy may become a habit. After forty-five years of hesitation it may require some personal experience of a compelling kind to break the crust. Some of those who know me best think that I ought to be more convinced than I am. Perhaps they are right."

In 1871 the late Lord Rayleigh married Evelyn, daughter of James Maitland Balfour, and sister of the Right Hon. Arthur Balfour. Mrs. Henry Sidgwick, who collaborated in his work on electrical standards, was his sister-in-law. In 1902 he was among the first recipients of the Order of Merit. In 1905 he was made a Member of the Privy Council. From

1892 to 1901 he acted as Lord Lieutenant of the County of Essex. In 1908 he succeeded the late Duke of Devonshire as Chancellor of the University of Cambridge. In 1904 he received—jointly with Sir William Ramsay—the Nobel Prize, the proceeds of which he presented to the University of Cambridge for an extension of the Cavendish Laboratory. It is needless to enumerate the scientific societies which elected him Honorary or Corresponding Member, or the Universities which conferred Honorary Degrees on him. The list would have to include all important scientific bodies in the world.

Among Rayleigh's achievements, the discovery of Argon is that which appeals most strongly to popular appreciation, yet it may be said with truth that his influence on scientific progress is independent of that discovery, which might be eliminated altogether without affecting our estimate of him as one of the greatest leaders of science in modern times. He had not the ambition to initiate revolutionary theories or to advance science by great and sudden strides. His procedure was to bring experiments into harmony with existing theories, to perfect those theories, if necessary, with the help of improved experimental methods, either by extending the range of accuracy or by new lines of investigation. His discovery of Argon was the natural outcome of this method of attack. It might be regarded as being a conspicuous ornament rather than the foundation of a reputation, to which no single incident could do more than add its contributive share.

In supreme devotion to science as well as in the exceptional combination of experimental and mathematical skill there is much resemblance between Rayleigh and Henry Cavendish, and the similarity extends to the advantages conferred by a social position that, in the early stages of a man's career, undoubtedly offers favourable opportunities. The contrast between the two men, therefore, becomes all the more striking when we compare their effective influence on the progress of science. Making due allowance for the inborn shyness of Henry Cavendish, there was an element of selfishness in his attitude which, so far as can be judged from the record of his life, can only be explained by an almost complete absence of human sympathy. Rayleigh's devotion to science was the reverse of selfish. By advice and encouragement he assisted every honest student of science. He liked to hear of the work of others and receive as well as impart information. The scientific discussions at the week-ends spent at Terling Place will always remain in the memory of those who had the advantage of taking part in them, and in the selection of his guests no other consideration ever entered except the common object of their interest in science. No one was ever a more lenient judge than Rayleigh. Even when he criticised he tried to find some mitigating circumstance that would excuse the errors committed, or some solitary idea of value in a work which he was forced to condemn as a whole. He disliked premature publication of discoveries, not only because they did not satisfy his own high standard, but because "scoffers"—as he expressed it—"would be encouraged."

The six volumes in which the record of his researches is collected remain a source of inspiration. The memorial tablet in Westminster Abbey will testify to the esteem of his countrymen, but those who have enjoyed his friendship and acquaintance will place above these tangible monuments the great example he set as a man: his magnanimity, his single-mindedness, the high ideals that have borne fruit in his generation, and may be expected to transmit their fertilising power on those who in years to come will have to carry the banner of science—a science that places humanity above material gain.

ARTHUR SCHUSTER.

EMIL FISCHER, 1852—1919.

WITHIN reasonable limits of space, and with due restraint of diction, it is difficult to convey an impression of the momentous influence exerted by Emil Fischer upon the chemistry and chemists of his generation. It is impossible to estimate the effect his work will produce in the thought and practice of his successors because, during the forty-five years of his activity, he not only enriched with a wealth of fresh examples and classified with unchallenged insight three fundamental groups of organic compounds, but in doing so he developed the technique and principles upon which is founded the modern science of biochemistry.

The preliminary step, taken in 1875, would then have appeared remote indeed from the goal. In that year he isolated phenylhydrazine from the product of reducing benzenediazonium chloride with potassium sulphite, and the variety of changes undergone by that substance immediately offered ample scope for his industry and ingenuity. During the intervals of studying these transformations he traced, in collaboration with his cousin, Otto Fischer, the hydrocarbon origin of rosaniline colouring matters, showing this to be triphenylmethane (1878), of which, or its homologues, the various eucanilines are triamino-derivatives.

It was in 1884 that Fischer discovered phenylglucosazone, produced by the concurrent dehydrogenation and condensation which take place when glucose or fructose is treated with phenylhydrazine. The significance of this observation lies in the fact that, although when purified the sugars may be crystallised without difficulty, they tend to remain obstinately amorphous when mixed; it follows that an agent which will serve to identify such materials in a sparingly soluble form is a weapon of the highest value in attacking problems involving them. Having demonstrated the utility of phenylhydrazine as a means of identification, he applied it to acrose, the syrup which he



EMIL FISCHER.

and Tafel obtained in 1887 from acrolein dibromide and baryta. This yielded two osazones— $C_{18}H_{22}O_4N_4$, corresponding to the synthetical sugars, α - and β -acrose; the former of these he identified with *dl*-fructose, whilst β -acrose has been since recognised as *dl*-sorbose. The discovery led to the first synthesis of naturally occurring sugars, and gave the definitive impulse to Fischer's work in the direction of biochemistry.

The procedure by which α -acrose became the source of synthetical *d*-glucose, *d*-mannose, and *d*-fructose depends on the observation (1890) that gluconic and mannonic acids are interconvertible when heated with quinoline at 140° . Applied in conjunction with Pasteur's method of resolving a racemic acid, and associated with the reduction of a polyhydroxylactone to the corresponding aldose, this principle not only enabled Fischer to synthesise the above-mentioned natural sugars, but, conjoined with the cyanhydrin synthesis, led to their optical antipodes and to the isolation of idose, gulose, and talose in their *d*-, *l*-, and *dl*-forms. Bringing the known hexoses into close review on the basis of Van't Hoff's theory, and assembling the sixteen possible projection formulæ in correlation with those of the eight possible aldopentoses, he proceeded (1891) to allocate the appropriate configuration to each individual, and subsequently (1896) confirmed the choice he had then made by degrading rhamnose to the corresponding methyltetrose and oxidising this to *d*-tartaric acid. Hence, amongst the sixteen optically active aldohexoses theoretically realisable, twelve have been either synthesised or configured, or both, by Fischer and his collaborators; his work on ribose caused *d*-allose and *d*-altrose to be added, and thus the *l*-forms of the two last-named sugars are now the only unknown members of the series. When it is recalled that in 1886 glucose and galactose were alone in the class of pentahydroxyaldehydes, and that the configuration of the four asymmetric carbon atoms was unrevealed, an appreciation of this opening achievement may be gained.

The naturally occurring glucosides, *e.g.*, amygdalin, indican, salicin, and myronic acid are amongst the earliest known compounds of organic origin, but little had been learned of their structure beyond the fact that they yield glucose on hydrolysis. In this sense several polysaccharides are glucosides for sucrose (cane-sugar), lactose, and raffinose all give hexose mixtures to which glucose is common, whilst maltose yields glucose alone. Synthesis of the first methylglucoside by Fischer (1893) was destined to elucidate the structure of glucosides in general, and ultimately to give new information respecting glucose itself. Followed by the discovery of an isomeride by Van Ekenstein (1894), it supported the butylene oxide formula for glucose which had been suggested by Tollens (1883). The α - and β -methylglucoside having been referred to corresponding forms of the parent hexose by E. F. Armstrong (1903), Simon's view (1901) of α - and β -glucose as lower homologues of α - and β -methylglucoside, respectively, was established. Interest in the subject was revived by Fischer's discovery of γ -methylglucoside (1914), with properties diverging from those of its isomerides sufficiently to justify the belief that it is an ethylene oxide, and although the corresponding γ -glucose

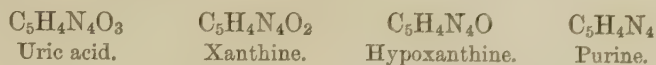
awaits isolation, the recognition of possible cyclic relations differing from that prevailing in α - and β -glucose has brought inquiry to the threshold of a new carbohydrate classification.

By means of glucose derivatives in which one hydroxyl group has been replaced by a halogen and the remaining ones acetylated, Fischer and his colleagues made concrete progress towards the synthesis of polysaccharides and natural glucosides. Whilst sucrose, the original aim of these experiments, was never produced by artificial means, a galactosidoglucose resembling melibiose, a glucosidogalactose differing from lactose, and a glucosidoglucose called *iso*-trehalose, were characterised. Similarly, in the direction of amygdalin synthesis, Fischer and Bergmann (1917) produced mandelonitrile- β -glucoside (sambunigrin and prulaurasin) in both active forms, followed by acetonecyanohydrin-glucoside (linamarin) and glycollonitrile-glucoside (1919), the simplest of the cyanogenetic glucosides.

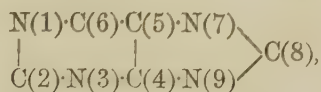
Although not strictly a glucoside, gallotannic acid, or gall-nut tannin, was shown by Strecker (1852) to yield glucose on hydrolysis; but the conflicting results of other chemists had led to the view, prevailing for half-a-century, that it is principally digallic acid. The latter, however, was synthesised by Fischer (1908) and found to be crystalline, although astringent, and having purified the main constituent of Chinese tannin, he obtained definite evidence (1912) that glucose does arise from this by hydrolysis. Improvement in the methods of acylation, necessarily a most difficult operation when involving such sensitive molecules as those of glucose and of digallic acid, enabled him in association with Bergmann (1918) to elaborate penta-(*m*-digalloyl)- α -glucose; the correspondence between potassium salts of this derivative, of Chinese tannin and of penta-(*m*-digalloyl)- β -glucose is so close as to establish the claim that the principal constituent of this form of tannin has been synthesised. The class-name "depside" had been introduced by Fischer and Freudenberg (1910) in application to those anhydrides of phenolcarboxylic acids in which condensation has occurred between the carboxyl of one molecule and the hydroxy-group of another; it was intended to emphasise the resemblance they bear towards tannins in behaviour and polypeptides or polysaccharides in structure, and thus Chinese tannin is elaborated from a glucose molecule in which five hydroxyl groups have been acylated by the depsidic nucleus, *m*-digalloyl.

During the years 1881-1899, Fischer conducted a sequence of investigations into uric acid and allied substances, adding a large number of synthetic products to the series and arranging the members of this important group in a rational system of classification. Uric acid was discovered in 1776, but it was not until 1834 that its composition was established; the constitutional formula advanced by Medicus in 1875 was confirmed by synthesis in 1888, but the relationship with xanthine and hypoxanthine had remained empirical. It appeared to Fischer that caffeine lent itself most readily to experimental treatment and it was consequently with this compound, in conjunction with xanthine, theobromine and guanine that a beginning was

made. Without following in detail the course of his numerous inquiries, it may be stated that his introduction of the word "purine" (1884) for the hypothetical parent of the series,



was most happily justified by the synthesis of purine itself (1898). Basing results upon his notation (1897) of the diureides as proceeding from the bicyclic nucleus



he succeeded at various times in establishing the constitution of xanthine (2:6-dioxypurine), hypoxanthine (6-oxypurine), adenine (6-amino-purine), guanine (2-amino-6-oxypurine), caffeine (1:3:7-trimethyl-2:6-dioxypurine), theophylline (1:3-dimethyl-2:6-dioxypurine) and theobromine (3:7-dimethyl-2:6-dioxypurine), uric acid being 2:6:8-trioxypurine.

Here again may be noticed the absorbing attraction presented to Fischer by the physiological aspect of the materials he selected for study. Purine derivatives include valuable drugs and comprise numerous compounds involved in animal and vegetable metabolism. The principles and processes which he developed in this field have gone far towards consolidating technical procedure in the Merck, Bayer, Höchst and Böhringer factories, whilst in collaboration with Von Mering (1903) he made a substantial contribution to manufacturing practice by an improvement in the production of diethylbarbituric acid, which led to that substance becoming one of the most valuable hypnotics in pharmacy under the name veronal.

The most important consequences of his gravitation towards biochemistry, however, arose from the fruitful inquiries which he made into the structure of proteins, and from the steps which he took in the direction of synthesising albuminoid molecules by associating into polypeptides their units of construction, the amino-acids. It had been recognised that many of these were obtainable from proteins by hydrolytic or enzymic disruption, and several had been synthesised in their racemic form: but Fischer, first suppressing their basic features by acylation (1899) and subsequently emphasising them by esterification (1900), devised practical methods for isolating the optically active modifications and for separating these from one another in complex mixtures. The direct result of these devices was to facilitate the recognition and estimation of component amino-acids in a great variety of natural proteins from widely different sources, of which silk-fibroin, amongst others, received his particular attention. By these means a number of representative amino-acids were assembled, and provided material for attempts to reconstruct the proteins from which they spring; the recognition of hippuric acid as benzoyl-glycine gave a clue to the form of union, and from this foundation a large

series of synthetic products, called "polypeptides" from their resemblance to peptones and, structurally, to polysaccharides, has been accumulated. One of these, an octadecapeptide (1907) composed of 15 glycine molecules and three of *l*-leucine, has the molecular weight, 1213: but refinement in the methods of preparation enabled Fischer to elaborate polypeptides from more diverse units, such as glycyl-*d*-alanyl-glycyl-*l*-tyrosine (1908), isomeric with the tetrapeptide obtained by silk-hydrolysis, and thus to present a link between the products of complex synthetical operations and the peptones arising from incomplete disruption of proteins.

Whilst the simpler polypeptides are crystalline, the tendency to amorphism increases with molecular weight; aqueous solutions of the more complex ones are opalescent, and yield precipitates with ammonium sulphate, phosphotungstic acid, and tannin, thus resembling the proteins themselves. Nevertheless, Fischer recognised the distant position occupied by the synthesis of natural proteins along the path he had begun to follow, because association of the monoamino-carboxylic acids glycine, alanine, valine, leucine, phenylalanine, tyrosine, serine, and cystine in the natural products is complicated by the presence of aspartic and glutamic acids with arginine, lysine, histidine, proline, and tryptophan.

Throughout these inquiries, Fischer made frequent and skilful use of enzymes, developing a technique which will offer invaluable guidance to subsequent investigators of vital changes. In 1894, having assembled a great variety of artificial carbohydrates, he studied their behaviour towards different families of yeast, drawing the fundamental conclusion that the fermentative enzyme is an asymmetric agent attacking only those molecules of which the configuration does not differ too widely from that of *d*-glucose. Applying this principle to the natural and artificial *d*-glucosides, he ranged these in two groups, the α -*d*-glucosides being hydrolysed by maltase and indifferent towards emulsin, the β -*d*-glucosides exhibiting converse behaviour. The *l*-glucosides, *d*-galactosides, arabinosides, xylosides, rhamnosides, and glucoheptosides were not affected by either enzyme, and the glucosidic relation of sucrose, maltose, and lactose was determined by similar means. It was the knowledge thus gained which led Fischer to represent enzyme-action by the analogy of a lock-and-key, and to conclude that disaccharides are fermented only as a consequence of preliminary hydrolysis.

Turning his attention to secretions of animal origin (1896), he studied the behaviour of carbohydrates and glucosides towards blood serum and a great variety of tissue-extracts and juices, but it was when those agents were applied by him, in association with Abderhalden (1903), to the proteins and polypeptides that the most fruitful results arose, from which it followed very clearly that the synthetic polypeptides are susceptible to zymolysis only when constructed of those amino-acids which occur in the natural proteins.

Emil Fischer was born on October 9, 1852, at Euskirchen. The only son of Laurenz Fischer and Julie Poensgen, he seemed destined for a career in

commerce, his father being a flourishing merchant and associated with his uncles in other ventures. Accordingly, on leaving school at Bonn in 1869, he was apprenticed to his brother-in-law, Ernst Friedrichs, a timber-merchant, but preference for experimental science led to his becoming a pupil of Kekulé in 1871. In the following year he proceeded from Bonn to Strasbourg, where he graduated in 1874 under Von Baeyer, passing with him to Munich in 1875. There he succeeded Volhard in 1879, and again in 1882 at Erlangen, whence Volhard had been called to Halle. On the transference of J. Wislicenus to Leipzig in 1885, he was appointed to the Chair of Chemistry at Würzburg, and, when Von Hofmann died in 1892, became Professor and Director of the Chemical Institute in the University of Berlin, occupying this post until his death, which took place in the night of July 14, 1919.

Even the remarkable diligence and insight which were his could not have enabled him to compass a field of achievement so vast, had he not possessed in full measure the quality of arousing enthusiasm in his collaborators, which followed inevitably from association with his kindling personality. Students from many nations were attracted to his laboratory in large numbers, and, although the prevailing atmosphere gave slender encouragement to aught else work, his quickening zeal did not fail to transform willing labourers into warm admirers. This was hastened by knowledge that his untiring singleness of purpose and somewhat austere manner were tempered by love of music, of art, and of joyous, human relaxation. His practice of concentration, stimulated at first by attachment to his chosen pursuit, was encouraged by the need to economise physical energy in consequence of suffering from the poisonous effect of mercury diethyl, and afterwards, more seriously, of phenylhydrazine; at a later period, absorption in work had to serve as a palliative to grief in the loss of his wife, Agnes Gerlach, who died in 1895, after a happy union of seven years' duration.

Fischer received the Davy Medal in 1890 and was elected a Foreign Member in 1899. He was awarded the Nobel Prize for Chemistry in 1902, and in 1907 delivered the Faraday Lecture before the Chemical Society, of which he had become an Honorary and Foreign Member in 1892. The address which he then gave, entitled "Synthetical Chemistry in its Relation to Biology," was a memorable synopsis of biochemical principles. Therein he traced the early connection between organic chemistry and those products of animal and vegetable life-processes which had provided Lavoisier, Gay-Lussac, Berzelius, and Liebig with material in elaborating the methods of chemical analysis; he showed how, later in the nineteenth century, organic chemistry had become separated from biology, the development of the subject by Liebig's famous pupils, Von Hofmann, Kekulé, and Wurtz, having proceeded on other lines, and he indicated the manner in which the association of the two subjects had become restored. Outlining a possible mechanism by which sugar may be produced from carbon dioxide through the agency of chlorophyll, he dwelt on the ignorance which still must be confessed

regarding synthesis of the fats from carbohydrates in plants or animals, and as to the manner in which they undergo combustion to carbon dioxide and water in the animal system. Finally, dealing with proteins, the most complicated of all materials concerned in cell-activity, he traced their relationship to peptones and amino-acids, explaining how the latter arise by various methods of hydrolysis and may be re-assembled into products which, in their simpler forms, resemble peptones, and even approach the proteins as their complexity increases. At appropriate points he emphasised the part played by enzymes in the catalytic changes which digestion and assimilation involve, the whole treatise constituting a powerful plea for renewing the alliance between chemistry and biology, an alliance which his own work has done more than that of any other chemist to cement.

The subjects to which Fischer mainly devoted his attention were not related directly to problems of manufacture, but he soon made contact with the chemical industry, and in 1883 was chosen to succeed Caro as Director of Research in the Badische factory. Although this most attractive offer was refused, he occupied towards the industrial leaders a very exceptional position, which was quite as much due to his own remarkable qualities as to the German system of linking science with technology. It was this which helped him to become instrumental in establishing the Kaiser-Wilhelm-Institut für Chemie, a foundation devoted to the pursuit of chemical research independently of teaching duties; the ceremony of opening the laboratories at Dahlem, Berlin, took place in October, 1912.

The variety of chemical issues engendered by the War absorbed his attention with increasing urgency until the last few months of his life. Foreseeing the effect of the blockade on the production of nitric acid from Chile saltpetre, he took part in the measures adopted for increasing the output of ammonia from coke-ovens and in the development of the synthetic nitric acid industry; but for the dimensions attained by the latter enterprise, Germany could not have continued the struggle after the middle of 1915. Problems connected with the need for augmenting the supplies of benzene and toluene, for utilising the sulphur-content of gypsum, and for seeking alternative sources of glycerine, also engrossed him in the earlier years; but it was the food-shortage, with all its physiological and psychological consequences, which ultimately became the most threatening element in the domestic situation. The commission appointed at his instigation explored the possibilities of straw, wood, leaves and rushes in supplying fodder for horses and cattle, and he devoted special attention to finding a coffee-substitute.

Burdened by these exacting labours and their distressing futility, his power of resistance to the malady from which he suffered became undermined. The eldest only of his three sons now survived, but the laboratory continued to be a source of mental distraction; in it he remained productively employed to the end. In view of the great age attained by his father, who lived to be 94, a period of activity longer than the 67 years

allotted to Emil Fischer might have been anticipated for him; but organic chemistry has never stimulated a more devoted follower, or been endowed more richly and permanently with the fruits of devotion to its pursuit.

Nevertheless, his roll of practical achievement is not the only basis for the admiration of his contemporaries. From boyhood a pronounced individualist, he rapidly acquired a grasp of essentials which, as he rose to eminence, gained him a position of unlimited influence amongst the scientific men of Germany. Trusting personalities more than organisations, and wisdom more than learning, his own magnetic personality and convincing wisdom were freely applied in the furtherance of scientific method, both industrial and academic. Whilst always in sympathy with the requirements of chemical industry—and herein lay one important factor of his authority—he placed the sound training of chemists, and the practice of investigation for its own sake, foremost in his creed. Such great qualities need to be recorded, because they tend to become obscured by the passage of years and the removal of those whom they inspired to action; but the glowing record of his additions to exact knowledge will remain undimmed by time.

M. O. F.

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Emil Fischer, 1.

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Palmer (W. G.) The Catalytic Activity of Copper—Part I, 13.

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Radiation in explosions of hydrogen and air (David), 183.

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Rayleigh (Lord). A Re-examination of the Light Scattered by Gases in respect of Polarisation.—II. Experiments on Helium and Argon, 57 ; — Double Refraction and Crystalline Structure of Silica Glass, 284.

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Sheppard (W. F.) Reduction of Error by Linear Compounding, 64.

Silberstein (L.) The Aspherical Nucleus Theory applied to the Balmer Series of Hydrogen, 1.

Silica glass, refraction and structure of (Rayleigh), 284.

Siren harmonics and pure-tone siren (Milne and Fowler), 414.

Slade (R. E.) and Higson (G. I.) Photochemical Investigations of the Photographic Plate, 154.

Soaps, ultramicroscopic structure of (Darke, McBain and Salmon), 395.

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Williams (A. M.) Forces in Surface Films. Part I.—Theoretical Considerations ; Part II.—Experimental Observations and Calculations ; Part III.—The Charge on Colloids, 223.

Williams (S. R.) See Hadfield, Williams and Bowen.

Wilson (E.) On the Measurement of Low Magnetic Susceptibility by an Instrument of New Type, 274.

Young (J. F. T.) See McLennan, Young and Ireton.

END OF THE NINETY-EIGHTH VOLUME (SERIES A).

MINUTES OF MEETINGS OF THE ROYAL SOCIETY.

January 22, 1920.

SPECIAL GENERAL MEETING.

Sir J. J. THOMSON, O.M., President, in the Chair.

H.R.H. the Prince of Wales (elected May 22, 1919) signed the obligation in the Charter Book, and was admitted into the Society.

Prof. W. H. Bragg, F.R.S., gave a discourse on Methods of Detecting Submarines by Sound.

January 22, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

In pursuance of the Statutes the names of Candidates for election into the Society were read as follows:—

Abell, Westcott Stile.	Douglas, Claude Gordon.
Agar, Wilfred Eade.	Douglas, Stewart Rankin.
Anderson, Alexander.	Dreyer, Georges.
Annandale, Nelson.	Eccles, William Henry.
Appleyard, Rollo.	Ewart, Alfred James.
Armstrong, Edward Frankland.	Farmer, Robert Crosbie.
Ashley, Sir William.	Fawcett, Edward.
Atkins, William Ringrose Gelston.	Flack, Martin William.
Bacot, Arthur William.	Francis, Francis Ernest.
Balfour, Andrew.	Gardner, John Addyman.
Beattie, James Martin.	Gemmell, James Fairlie.
Berry, Arthur.	Greenwood, Major.
Bond, Charles John.	Groom, Percy.
Borradaile, Lancelot Alexander.	Gunn, James Andrew.
Bose, Sir Jagadis Chunder.	Harmer, Frederic William.
Broom, Robert.	Hartley, Harold.
Bryce, Thomas Hastie.	Henderson, James B.
Buckmaster, George Alfred.	Herring, Percy Theodore.
Burnside, William Snow.	Hill, Arthur William.
Bury, Henry.	Hilton, Harold.
Calman, William Thomas.	Horrocks, William Heaton.
Campbell, Albert.	Houston, Alexander Cruikshank.
Cathcart, Edward Provan.	Hoyle, William Evans.
Chapman, Alfred Chaston.	Hume, William Frazer.
Chattock, Arthur Prince.	Hutchinson, Arthur.
Church, Arthur Henry.	Jackson, Louis Charles.
Cole, Frank Joseph.	Jeffrey, Edward Charles.
Davidson, Charles Rundle.	Jones, Frederic Wood.
Davison, Charles.	Knott, Cargill Gilston.
Desch, Cecil H.	Lake, Philip.
Denny, Sir Archibald.	Lanchester, Frederick William

Lawson, Abercrombie Anstruther.	Plimmer, Robert Henry Aders.
Leathem, John Gaston.	Plummer, Henry Crozier.
Ledingham, John Charles Grant.	Price, Thomas Slater.
Leiper, Robert Thomson.	Procter, Henry Richardson.
Lindemann, Frederick Alexander.	Rây, Sir Prafulla Chandra.
Locke, Frank Spiller.	Reed, Frederick Richard Cowper.
McCarrison, Robert.	Ridewood, Walter George.
MacLeod, John J. Rickard.	Ritchie, James.
Mallik, Devendra Nath.	Robinson, Arthur.
Marshall, Francis Hugh Adam.	Robinson, Robert.
Marshall, Guy Anstruther Knox.	Russell, Alexander.
Maw, William Henry.	Schryver, Samuel Barnett.
Mawson, Sir Douglas.	Shaw, Philip Egerton.
Mellor, Joseph William.	Silberrad, Oswald.
Merton, Thomas Ralph.	Skeats, Ernest Willington.
Middlemiss, Charles Stewart.	Smith, Sir Frederick.
Mill, Hugh Robert.	Smith, Sir William Edward.
Milner, Samuel Roslington.	Spearman, Charles.
Milroy, Thomas Hugh.	Spencer, Leonard James.
Moss, Charles Edward.	Stephens, John William Watson.
Mummery, John Howard.	Thornton, William Mundell.
Ogilvie-Grant, William Robert.	Vernon, Horace Middleton.
Orton, Kennedy Joseph Previté.	Vickers, Albert.
Parsons, John Herbert.	Watson, David Meredith Seares.
Parsons, Hon. Richard Clere.	Whytlaw-Gray, Robert.
Patterson, Thomas Stewart.	Willcox, William Henry.
Perkins, Robert Cyril Layton.	Wilson, Ernest.
Philip, James Charles.	Yarrow, Sir Alfred Fernandez.

The following Papers were read :—

- I. "The Stress-Strain Properties of Nitro-Cellulose and the Laws of its Optical Behaviour." By E. G. COKER, F.R.S., and K. C. CHAKKO.
- II. "On Alternating Current Electrolysis." By S. MARSH. Communicated by Prof. E. H. GRIFFITHS, F.R.S.
- III. "The Variations of Wave-Length of the Oscillations Generated by Three-Electrode Thermionic Tubes due to Changes in Filament Current, Plate Voltage, Grid Voltage, or Coupling." By W. H. ECCLES and J. H. VINCENT. Communicated by Prof. W. H. BRAGG, F.R.S.
- IV. "Plane Strain.—The Direct Determination of Stress." By S. D. CAROTHERS. Communicated by Prof. A. E. H. LOVE, F.R.S.

- V. "An Investigation of the Effects of Electron Collisions with Platinum and with Hydrogen, to ascertain whether the Production of Ionisation from Platinum is due to Occluded Hydrogen." By F. HORTON and A. C. DAVIES. Communicated by C. T. R. WILSON, F.R.S.
- VI. "The Pressure Distribution on the Head of a Shell Moving at High Velocities." By L. BAIRSTOW, F.R.S., R. H. FOWLER, and D. R. HARTREE.

January 29, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following Papers were read :—

- I. "The Genetics of 'Rogues' among Culinary Peas (*Pisum Sativum*). By W. BATESON, F.R.S.
- II. "Studies on Synapsis.—I. Oogenesis in the Hymenoptera." By L. T. HOGBEN. Communicated by Prof. E. W. MACBRIDE, F.R.S.
- III. "On a Periodic Structure in many Insect Scales, and the Cause of their Iridescent Colours." By H. ONSLOW. Communicated by Prof. F. G. HOPKINS, F.R.S.

February 5, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

Meeting for Discussion.

Subject: The Theory of Relativity. Discussion opened by Mr. J. H. JEANS, Sec. R.S.

February 12, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following Papers were read :—

- I. "Colloidal Electrolytes.—Soap Solutions and their Constitution." By J. W. MCBAIN and C. S. SALMON. Communicated by Prof. S. YOUNG, F.R.S.

- II. "On the Viscosity of Sulphur." By C. C. FARR and D. B. MACLEOD. Communicated by Dr. C. CHREE, F.R.S.
- III. "On Kaufmann's Theory of the Impact of the Pianoforte Hammer." By C. V. RAMAN and B. BANERJI. Communicated by Dr. G. T. WALKER, C.S.I., F.R.S.
- IV. "On a Theory of the Second Order Longitudinal Spherical Aberration for a Symmetrical Optical System." By Commander T. Y. BAKER, R.N., and Prof. L. N. G. FILON, F.R.S.
- V. "The Lateral Vibrations of Sharply Pointed Bars." By Prof. J. W. NICHOLSON, F.R.S.
- VI. "A New Method of Spectro-photometry in the Visible and Ultra-violet and the Absorption of Light by Silver Bromide." By R. E. SLADE and F. C. TOY. Communicated by Sir HERBERT JACKSON, K.B.E., F.R.S.
- VII. A "Note on Dr. Chree's Discussion of Two Magnetic Storms." By Dr. S. CHAPMAN, F.R.S.
- VIII. "An Explanation of the Criticisms on Dr. Chapman's recent Paper: 'An Outline of a Theory of Magnetic Storms.'" By Dr. C. CHREE, F.R.S.

February 19, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following Papers were read:—

- I. "Studies of Photo-synthesis in Fresh-water Algæ.—1. The Fixation of Both Carbon and Nitrogen from the Atmosphere to form Organic Tissue by the Green Plant Cell. 2. Nutrition and Growth produced by High Gaseous Dilutions of Simple Organic Compounds, such as Formaldehyde and Methylic Alcohol. 3. Nutrition and Growth by means of High Dilutions of Carbon Dioxide and Oxides of Nitrogen, without Access to Atmosphere." By B. MOORE, F.R.S., and T. A. WEBSTER.
 - II. "The Properties of Colloidal Systems. IV.—Reversible Gelation in Living Protoplasm." By W. M. BAYLISS, F.R.S.
 - III. "The Development of the Auditory Apparatus in *Sphenodon punctatus*." By F. J. WYETH. Communicated by Prof. A. DENDY, F.R.S.
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February 26, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

In pursuance of the Statutes, the names of the Candidates recommended for election into the Society were read from the Chair as follows :—

Armstrong, E. F.	Knott, C. G.
Bose, Sir J. C.	Lindemann, F. A.
Broom, R.	Marshall, F. H. A.
Cathcart, E. P.	Merton, T. R.
Chapman, A. C.	Perkins, R. C. L.
Chattock, A. P.	Plummer, H. C.
Hill, A. W.	Robinson, R.
Stephens, J. W. W.	

The following Papers were read :—

- I. "Some Measurements of Atmospheric Turbulence." By L. F. RICHARDSON. Communicated by Sir NAPIER SHAW, F.R.S.
- II. "The Pressure upon the Poles of Metallic Arcs, including Alloys and Composite Arcs." By W. G. DUFFIELD, T. H. BURNHAM, and A. A. DAVIS. Communicated by Prof. O. W. RICHARDSON, F.R.S.
- III. "On the Viscosities and Compressibilities of Liquids at High Pressure." By J. H. HYDE. Communicated by Prof. J. E. PETAVEL, F.R.S.
- IV. "The Capacity Coefficients of Spherical Conductors." By A. RUSSELL. Communicated by Dr. C. CHREE, F.R.S.
- V. "On the Refraction and Dispersion of Carbon Dioxide, Carbon Monoxide, and Methane." By C. CUTHBERTSON, F.R.S., and MAUDE CUTHBERTSON.
- VI. "The Phenomena of Rupture and Flow in Solids." By A. A. GRIFFITH. Communicated by G. I. TAYLOR, F.R.S.

March 4, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following Papers were read :—

- I. "The Protoplasmic Factor in Photo-synthesis." By Dr. F. F. BLACKMAN, F.R.S.

- II. "The Beginning of Photo-synthesis in the Green Leaf." By G. E. BRIGGS. Communicated by Dr. F. F. BLACKMAN, F.R.S.
- III. "Sunlight and the Life of the Sea. (Studies of the Photo-synthesis in Marine Algæ: (1) Fixation of Carbon and Nitrogen from Inorganic Sources in Sea-water; (2) Increase of Alkalinity of Sea-water as a Result of Photo-synthesis and as a Measure of that Process; (3) Relative Photo-synthetic Activity of Green, Brown, and Red Sea-weeds in Light of Varying Intensity)." By Dr. BENJAMIN MOORE, F.R.S., E. WHITLEY, and T. A. WEBSTER.
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March 11, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following papers were read:—

- I. "The Pressure upon the Poles of Metallic Arcs, including Alloys and Composite Arcs." By W. G. DUFFIELD, T. H. BURNHAM, and A. A. DAVIS. Communicated by Prof. O. W. RICHARDSON, F.R.S.
- II. "Further Experiments on the Variation of Wave-Length of the Oscillations Generated by an Ionic Valve due to Changes in Filament Current." By J. H. VINCENT. Communicated by Prof. W. H. BRAGG, C.B.E., F.R.S.
- III. "The Theory of the Katharometer." By H. A. DAYNES. Communicated by Prof. S. W. J. SMITH, F.R.S.
- IV. "The Process of Diffusion through a Rubber Membrane." By H. A. DAYNES. Communicated by Prof. S. W. J. SMITH, F.R.S.
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March 18, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following papers were read:—

- I. "On a Form of *Betrytis cinerea* with Colourless Sclerotia." By W. B. BRIERLEY. Communicated by Dr. E. J. RUSSELL, F.R.S.
- II. "A Preliminary Account of the Meiotic Phenomena in the Pollen Mother-cells and Tapetum of Lettuce (*Lactuca sativa*)." By R. R. GATES. Communicated by Prof. J. B. FARMER, F.R.S.
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March 25, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following papers were read:—

- I. "Note on the Central Differential Equation in the Relativity Theory of Gravitation." By A. R. FORSYTH, F.R.S.
- II. "The Frequency of Earthquakes in Italy in the Years 1896 to 1914." By R. D. OLDHAM, F.R.S.
- III. "A New Apparatus for Drawing Conic Curves." By A. F. DUFTON. Communicated by Mr. C. V. BOYS, F.R.S.
- IV. "An Experimental Determination of the Distribution of the Partial Correlation Coefficient in Samples of Thirty." By Capt. J. W. BISPHAM, R.E. Communicated by Dr. C. J. MARTIN, F.R.S.

The Society adjourned over the Easter Recess to Thursday, April 22.

April 22, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following Papers were read:—

- I. "Experiments on the Pressure Wave thrown out by Submarine Explosions." By H. W. HILLIAR. Communicated by Prof. J. C. McLENNAN, F.R.S.
- II. "A Study of the Catalytic Action at Solid Surfaces. III.—The Hydrogenation of Acetaldehyde and the Dehydrogenation of Ethyl Alcohol in the Presence of Finely Divided Metals." By E. F. ARMSTRONG and T. P. HILDITCH. Communicated by Prof. H. E. ARMSTRONG, F.R.S.
- III. "A Study of the Catalytic Action at Solid Surfaces. IV.—The Interaction of Carbon Monoxide and Steam as Conditioned by Iron Oxide and by Copper." By E. F. ARMSTRONG and T. P. HILDITCH. Communicated by Prof. H. E. ARMSTRONG, F.R.S.
- IV. "On the Structure of the Balmer Series of Hydrogen Lines." By T. R. MERTON, D.Sc. Communicated by Prof. A. FOWLER, F.R.S.
- V. "Diamagnetism Due to Free Electrons." By Prof. H. A. WILSON, F.R.S.

April 29, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following Papers were read :—

- I. "The Irish Eskers." By Prof. J. W. GREGORY, F.R.S.
 - II. "The Life-History and Cytology of *Synchytrium endobioticum* (Schilb.) Perc., the Cause of Wart Disease in Potato." By Miss K. M. CURTIS. Communicated by Prof. V. H. BLACKMAN, F.R.S.
 - III. "On the Structure and Affinities of *Acromyza pancheri*, Pilger." By B. SAHNI. Communicated by Prof. A. C. SEWARD, F.R.S.
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May 6, 1920.

Sir J. J. THOMSON, O.M., President, followed by Sir NAPIER SHAW, in the Chair.

The following Papers were read :—

- I. "The Aerodynamics of a Spinning Shell." By R. H. FOWLER, E. C. GALLOP, C. N. H. LOCK, and H. W. RICHMOND, F.R.S.
 - II. "Researches on the Elastic Properties and the Plastic Extension of Metals." By Prof. W. E. DALBY, F.R.S.
 - III. "Investigations on Lightning Discharges and on the Electric Field of Thunderstorms." By C. T. R. WILSON, F.R.S.
 - IV. "The Supply of Energy to Atmospheric Eddies." By L. F. RICHARDSON. Communicated by Sir NAPIER SHAW, F.R.S.
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May 13, 1920.

Annual Meeting for the Election of Fellows.

Sir J. J. THOMSON, O.M., President, in the Chair.

The Statutes relating to the Election of Fellows having been read, Prof. Vines and Prof. Fowler were, with the consent of the Society, nominated Scrutators, to assist the Secretaries in the examination of the balloting lists.

The votes of the Fellows present were collected, and the following candidates were declared duly elected into the Society :—

Armstrong, E. F.	Knott, C. G.
Bose, Sir J. C.	Lindemann, F. A.
Broom, R.	Marshall, F. H. A.
Cathcart, E. P.	Merton, T. R.
Chapman, A. C.	Perkins, R. C. L.
Chattock, A. P.	Plummer, H. C.
Hill, A. W.	Robinson, R.
Stephens, J. W. W.	

May 13, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following Papers were read :—

- I. "Demonstration of the Apparent 'Growth' of Plants (and of Inanimate Materials) and of their Apparent 'Contractility.'" By Dr. A. D. WALLER, F.R.S.
- II. "On the 'Renal Portal' System (Renal Venous Meshwork) and Kidney Excretion in Vertebrata." By W. N. F. WOODLAND. Communicated by Prof. A. KEITH, F.R.S.

May 20, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

Sir J. C. Bose, Mr. A. C. Chapman, Mr. A. W. Hill, Dr. F. H. A. Marshall, Prof. T. R. Merton, Prof. H. C. Plummer, and Prof. J. W. W. Stephens, were admitted into the Society.

The following Papers were read :—

- I. "Some Notes on Krypton and Xenon." By Prof. J. N. COLLIE, F.R.S.
- II. "Experiments on Electron Emission from Hot Bodies." By SIH LING TING. With a Preface by Prof. O. W. RICHARDSON, F.R.S.
- III. "The Aspherical Nucleus Theory applied to the Balmer Series of Hydrogen." By L. SILBERSTEIN. Communicated by Prof. J. W. NICHOLSON, F.R.S.
- IV. "On the Conditions at the Boundary of a Fluid in Turbulent Motion." By T. E. STANTON, F.R.S., Miss D. MARSHALL, and Mrs. C. N. BRYANT.

The Society adjourned over the Whitsun Recess to Thursday, June 3.

June 3, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

Dr. E. F. Armstrong, Prof. E. P. Cathcart, Dr. A. P. Chattock, Prof. F. A. Lindemann, and Prof. R. Robinson, were admitted into the Society.

THE BAKERIAN LECTURE—"The Nuclear Constitution of the Atom"—was delivered by Sir ERNEST RUTHERFORD, F.R.S.

June 10, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

Dr. C. G. Knott and Mr. R. Perkins were admitted into the Society.

The following Papers were read:—

- I. "The Thermo-elastic Properties of Muscle." By A. V. HILL, F.R.S., and W. HARTREE.
 - II. "The Absorption of Light by Elements in the State of Vapour: Selenium and Tellurium" By Sir JAMES DOBBIE, F.R.S., and J. J. FOX.
 - III. "The Absorption of Light by Elements in the State of Vapour: Mercury, Cadmium, Zinc, Phosphorus, Arsenic, Antimony." By Sir JAMES DOBBIE, F.R.S., and J. J. FOX.
 - IV. "Monoclinic Double Selenates of the Copper Group." By A. E. H. TUTTON, F.R.S.
 - V. "Production and Transmission of an Environmental Effect in *Simocephalus vetulus*." By H. G. CANNON. Communicated by Prof. E. W. MCBRIDE, F.R.S.
 - VI. "The Enzymes of *B. coli communis*, which are concerned in the Decomposition of Glucose and Manitol. Part IV.—The Fermentation of Glucose in the Presence of Formic Acid." By E. C. GREY. Communicated by Prof. F. G. HOPKINS, F.R.S.
 - VII. "Studies on Synapsis. II.—Parallel Conjugation and the Prophase Complex in Periplaneta, with Special Reference to the Premeiotic Telophase." By L. T. HOGBEN. Communicated by Prof. E. W. MCBRIDE, F.R.S.
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June 17, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

THE CROONIAN LECTURE—"Genetic Segregation"—was delivered by Prof. WILLIAM BATESON, F.R.S.

June 24, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

The following Papers were read :—

- I. "On some Rostro-carinate Flint Implements and Allied Forms." By Sir RAY LANKESTER, K.C.B., F.R.S.
- II. "A Re-examination of the Light Scattered by Gases in respect of Polarization. I.—Experiments on the Common Gases." By LORD RAYLEIGH, F.R.S.
- III. "Note on the Influence of Temperature on the Rigidity of Metals." By A. MALLOCK, F.R.S.
- IV. "A Study of Catalytic Actions at Solid Surfaces. V.—The Rate of Change Conditioned by a Nickel Catalyst and its Bearing on the Law of Mass Action." By E. F. ARMSTRONG, F.R.S., and T. P. HILDITCH, D.Sc.
- V. "Tidal Friction in Shallow Seas." By H. JEFFREYS, D.Sc. Communicated by Sir NAPIER SHAW, F.R.S.
- VI. "Electrification of an Insulated Lens and Allied Problems treated by the Stream Function." By Sir GEORGE GREENHILL, F.R.S.
- VII. "Simultaneous Values of Magnetic Declination at different British Stations." By CHARLES CHREE, F.R.S.
- VIII. "Arc Spectra *in vacuo* and Spark Spectra in Helium of various Elements." By Prof. J. C. McLENNAN, F.R.S., J. F. T. YOUNG, and H. J. C. IRETON.
- IX. "Spark Spectra of various Elements in Helium in the extreme Ultra-Violet." By Prof. J. C. McLENNAN, F.R.S., and A. C. LEWIS.
- X. "Low Voltage Ionization Phenomena in Mercury Vapour." By K. H. KINGDON. Communicated by Prof. J. C. McLENNAN, F.R.S.
- XI. "Symmetrisable Functions and their Expansion in Terms of Biorthogonal Functions." By J. MERCER, D.Sc. Communicated by Prof. E. W. HOBSON, F.R.S.

- XII. "Reduction of Error by Linear Compounding." By W. F. SHEPPARD. Communicated by Prof. E. T. WHITTAKER, F.R.S.
- XIII. "Plane Stress and Plane Strain in Bipolar Co-ordinates." By G. B. JEFFREY. Communicated by Prof. L. N. G. FILON, F.R.S.
- XIV. "The Tidal Motion in the Irish Sea: its Currents and its Energy." By R. O. STREET. Communicated by Sir JOSEPH LARMOR, F.R.S.
- XV. "The Catalytic Activity of Copper.—Part I." By W. G. PALMER. Communicated by Sir WILLIAM POPE, F.R.S.
- XVI. "The Origin of the 'Cyanogen' Bands." By S. BARRATT. Communicated by Prof. T. R. MERTON, F.R.S.
- XVII. "The Effects of Electron Collisions with Atmospheric Neon." By F. HORTON, Sc.D., and ANN C. DAVIES. Communicated by Mr. C. T. R. WILSON, F.R.S.
- XVIII. "On the Occurrence of Diatoms on the Skin of Whales." By A. G. BENNETT. With an Appendix by E. W. NELSON. Communicated by Sir SIDNEY HARMER, F.R.S.
- XIX. "An Extension of the Balmer Series of Hydrogen and Spectroscopic Phenomena of very Long Vacuum Tubes." By R. W. WOOD, For. Mem. R.S.
- XX. "Moving Striations in Neon and Helium." By F. W. ASTON, D.Sc., and T. KIKUCHI. Communicated by Sir ERNEST RUTHERFORD, F.R.S.

The Society adjourned over the Long Vacation to Thursday, November 4.

November 4, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

Sir James Frazer was admitted into the Society.

The following papers were read :—

- I. "On the Vibrations of an Elastic Plate in Contact with Water." By Prof. H. LAMB, F.R.S.
- II. "The Transmission of Electric Waves around the Earth's Surface." By Prof. H. M. MACDONALD, F.R.S.
- III. "A Re-examination of the Light Scattered by Gases in respect of Polarization.—II. Experiments on Helium and Argon." By LORD RAYLEIGH, F.R.S.

- IV. "Dilatation and Compressibility of Liquid Carbonic Acid." By Prof. C. F. JENKIN. Communicated by Sir J. A. EWING, F.R.S.
- V. "Radiation in Explosions of Hydrogen and Air." By W. T. DAVID. Communicated by Prof. H. L. CALLENDAR, F.R.S.
- VI. "Photochemical Investigations of the Photographic Plate." By R. E. SLADE, D.Sc., and G. I. HIGSON. Communicated by Prof. J. N. COLLIE, F.R.S.
- VII. "The Relationship between Pressure and Temperature at the same Level in the Free Atmosphere." By E. H. CHAPMAN, D.Sc. Communicated by Sir NAPIER SHAW, F.R.S.
- VIII. "Note on Vacuum Grating Spectroscopy." By Prof. J. C. McLENNAN, F.R.S.

November 11, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

Sir G. P. Lenox Conyngham (elected 1918) was admitted into the Society.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair.

The following papers were read :—

- I. "On the Calcification of the Vertebral Centra in Sharks and Rays." By W. G. RIDWOOD, D.Sc. Communicated by Prof. E. W. MACBRIDE, F.R.S.
- II. "Studies in the Mechanism of Enzyme Action.—I. Rôle of the Reaction of the Medium in Fixing the Optimum Temperature of a Ferment." By A. COMPTON, D.Sc. Communicated by Prof. B. MOORE, F.R.S.
- III. "The Effect of Certain Dietary Deficiencies on the Suprarenal Glands." By C. H. KELLAWAY. Communicated by W. B. HARDY, Sec. R.S.
- IV. "The Genetics of Sex in *Funaria hygrometrica*." By E. J. COLLINS. Communicated by W. BATESON, F.R.S.

November 18, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

The Right Hon. Viscount Grey of Fallodon (elected 1914) was admitted into the Society.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair.

The following Papers were read :—

- I. "On the Absorption and Scattering of Light." By Sir ARTHUR SCHUSTER, F.R.S.
- II. "The Emission of Electrons under the Influence of Chemical Action." By Prof. O. W. RICHARDSON, F.R.S.
- III. "Magnetism and Atomic Structure.—I." By A. E. OXLEY, D.Sc. Communicated by Prof. S. CHAPMAN, F.R.S.
- IV. I.—"On the Proximity of Atoms in Gaseous Molecules. II.—On the Similarity between Carbon Dioxide and Nitrous Oxide." By Prof. A. O. RANKINE. Communicated by Prof. H. L. CALLENDAR, F.R.S.
- V. "Forces in Surface Films. Part I.—Theoretical Considerations. Part II.—Experimental Observations and Calculations. Part III.—The Charge on Colloids." By A. M. WILLIAMS, D.Sc. Communicated by Prof. J. WALKER, F.R.S.

November 25, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

A Special General Meeting of the Society was held to receive the Annual Report of the Council.

November 25, 1920.

Sir J. J. THOMSON, O.M., President, in the Chair.

In pursuance of the Statutes, notice of the ensuing Anniversary Meeting was given from the Chair, and the List of Officers and Council nominated for election was read as follows :—

President.—Prof. Charles Scott Sherrington, M.A., M.D.

Treasurer.—Sir David Prain, C.M.G., C.I.E.

Secretaries.— $\left\{ \begin{array}{l} \text{William Bate Hardy, M.A.} \\ \text{James Hopwood Jeans, M.A.} \end{array} \right.$

Foreign Secretary.—Sir Arthur Schuster, Sc.D.

Other Members of the Council.—Joseph Barcroft, C.B.E. ; Sir William Bragg, K.B.E., D.Sc. ; Prof. Arthur William Crossley, C.M.G., D.Sc. ; Prof. John Bretland Farmer, M.A. ; Sir Walter Morley Fletcher, K.B.E. ; Prof. Alfred Fowler ; Alfred Cort Hadden, Sc.D. ; Sir Robert Abbott Hadfield, Bart. ; Sir Thomas Little Heath, K.C.B., K.C.V.O., Sc.D. ; Prof. John Graham Kerr, M.A. ; Prof. Horace Lamb, Sc.D. ; Sir William Boog Leishman, K.C.M.G., C.B., M.B. ; Sidney Harris Cox Martin, M.D. ; Prof. John William Nicholson, D.Sc. ; Richard Dixon Oldham ; Prof. William Palmer Wynne, D.Sc.

The following papers were read :—

- I. "The Growth of Seedlings in Wind." By Prof. LEONARD HILL, F.R.S.
- II. "The Effect of Thyroid-feeding and of Thyro-parathyroidectomy upon the Pituitrin Content of the Posterior Lobe of the Pituitary, the Cerebro-spinal Fluid, and Blood." By Prof. P. T. HERRING. Communicated by Sir E. SHARPEY SCHAFER, F.R.S.
- III. "Reflex Times in the South African Clawed Frog." By W. A. JOLLY. Communicated by Sir E. SHARPEY SCHAFER, F.R.S.
- IV. "Cellular Immunity: Observations on Natural and Acquired Immunity to Cobra Venom." By Prof. J. A. GUNN and R. ST. A. HEATHCOTE. Communicated by Prof. C. S. SHERRINGTON, F.R.S.
- V. "Studies on Synapsis.—III. The Nuclear Organisation of the Germ Cells in *Libellula depressa*." By L. T. HOGBEN. Communicated by Prof. E. W. MACBRIDE, F.R.S.

November 30, 1920.

ANNIVERSARY MEETING.

Sir J. J. THOMSON, O.M., President, in the Chair.

The Report of the Auditors of the Treasurer's accounts was read, and the thanks of the Society were given to the Treasurer and to the Auditors.

The List of Fellows deceased and the List of Fellows elected into the Society since the last Anniversary were read.

The Report to the Society from the Council, upon the work during the past year, was, upon the motion of the President, received.

The President delivered his Anniversary Address. On the motion of Dr. S. Martin, seconded by Sir J. Dobbie, the thanks of the Society were voted to the President for his Address, and he was requested to allow it to be printed.

The Awards of the Medals for the year were announced as follows, and the Medals were presented from the Chair :—

The Copley Medal	To Mr. Horace T. Brown.
The Rumford Medal	„ Lord Rayleigh.
A Royal Medal	„ Mr. W. Bateson.
A Royal Medal	„ Prof. G. H. Hardy.
The Davy Medal	„ Mr. C. T. Heycock.
The Darwin Medal	„ Prof. R. H. Biffen.
The Hughes Medal	„ Prof. O. W. Richardson.

The President having, with the consent of the Society, nominated Sir Frank Dyson and Prof. W. M. Bayliss as Scrutators to examine the balloting lists for the election of Council and Officers, the votes of the Fellows present were taken.

The Scrutators reported that the Council and Officers nominated at the preceding meeting had been duly elected.

The thanks of the Society were given to the Scrutators.

December 9, 1920.

Prof. C. S. SHERRINGTON, President, in the Chair.

Dr. W. D. Matthew (elected 1919) was admitted into the Society.

The following Papers were read:—

- I. "Double Refraction and Crystalline Structure of Silica Glass." By LORD RAYLEIGH, F.R.S.
- II. "The Effect of Asymmetry on Wave-length Determinations." By Prof. J. W. NICHOLSON, F.R.S., and Prof. T. R. MERTON, F.R.S.
- III. "On the Effect of Concentration on the Spectra of Luminous Gases." By Prof. T. R. MERTON, F.R.S.
- IV. "On the Measurement of Low Magnetic Susceptibility by an Instrument of New Type." By Prof. E. WILSON. Communicated by Prof. J. W. NICHOLSON, F.R.S.
- V. "The Internal Energy of Inflammable Mixtures of Coal-gas and Air after Explosion." By Prof. W. T. DAVID. Communicated by Sir DUGALD CLERK, F.R.S.
- VI. "Multenions and Differential Invariants." By Prof. A. MCAULAY. Communicated by Mr. W. B. HARDY, Sec. R.S.

The Society adjourned over the Christmas Recess to Thursday, January 20, 1921.
